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DEPARTMENT OF ORGANIC CHEMISTRY
THE POLYMER GROUP

ON THE THERMAL AND THERMO-OXIDATIV DEGRADATION OF POLYETHYLENE

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GÖTEBORG 1973

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TO

THE SEA

AND

MY FAMILY

ON THE THERMAL AND THERMO-OXIDATIVE DEGRADATION OF POLYETHYLENE

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This thesis is based on the following papers:

I. A. Holmström and E. Sörvik

Thermal Degradation of Polyethylene in a Nitrogen Atmosphere of Low Oxygen Content
I. Changes in Molecular Weight Distribution

J. Chrom., 53, 95 (1970)

II. A. Holmström and E.M. Sörvik

Thermal Degradation of Polyethylene in a Nitrogen Atmosphere of Low Oxygen Content
II. Structural Changes Occuring in Low-Density Polyethylene at an Oxygen Content Less than 0.0005 %

J. Appl. Polym. Sci., In press

III. A. Holmström and E.M. Sörvik

Thermal Degradation of Polyethylene in a Nitrogen Atmosphere of Low Oxygen Content
III. Structural Changes Occuring is Low-Density Polyethylene at Oxygen Contents Below 1.2 %

J. Appl. Polym. Sci., In press

In the following text these works are referred to as I-III.

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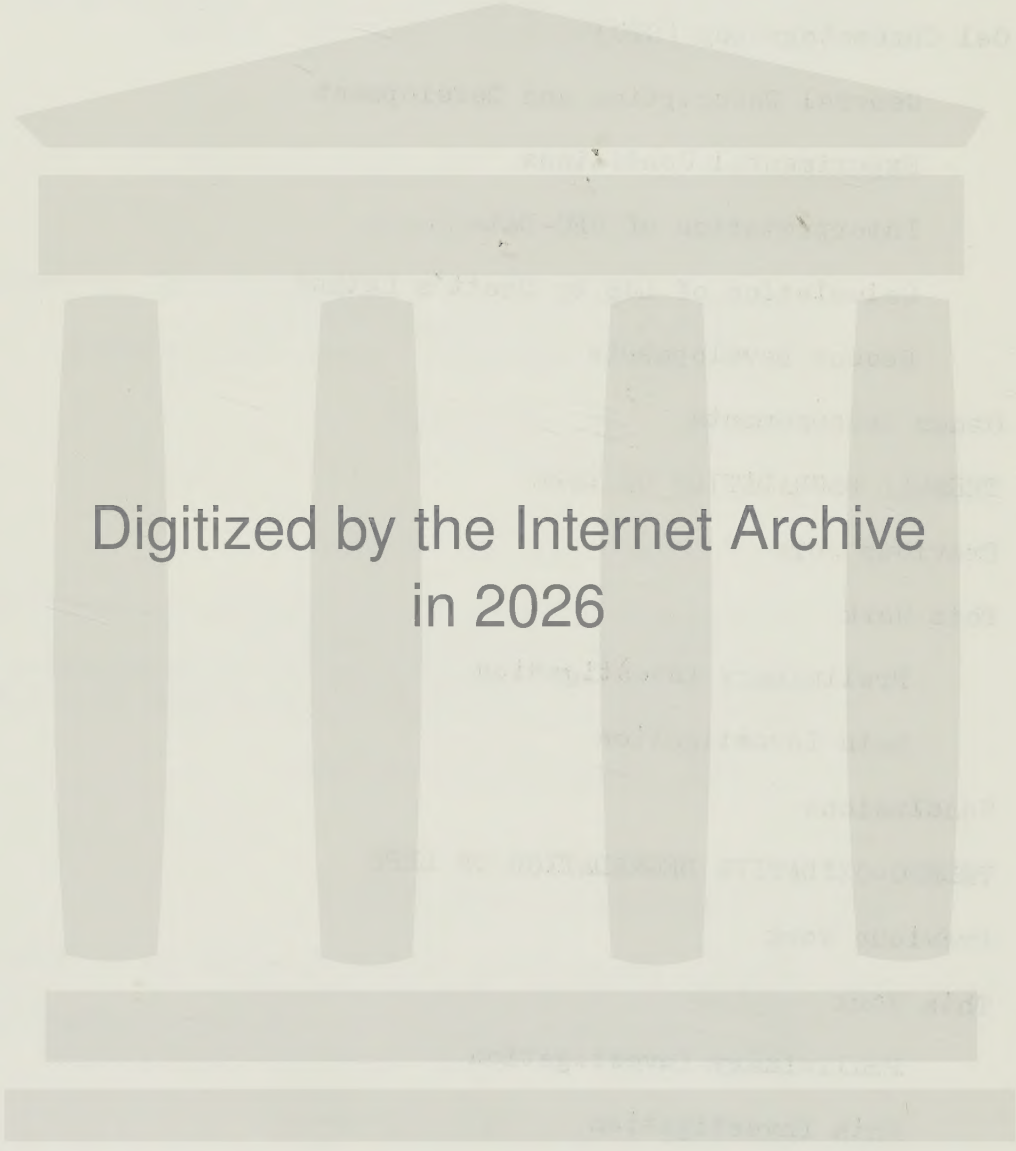
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SUMMARY

The thermal and thermo-oxidative degradation of low-density polyethylene (LDPE) have been studied.
Contrary to earlier statements concerning the thermal degradation it was found that polyethylene (PE) is not degraded according to a random scission type of mechanism. Instead both chain scission and molecular enlargement are found to occur simultaneously. At 315°C and below the molecular enlargement reactions were found to dominate while chain scission dominated at 333°C and above.

The samples were heated at temperatures between 284 and 355°C under high purity grade nitrogen in the thermal degradation and under nitrogen containing up to 1.16 % oxygen in the thermo-oxidative degradation. Changes in molecular weight distribution (MWD) and degree of long chain branching (LCB) were followed by gel chromatography (GPC) and viscosity measurements. Other structural changes were investigated by infrared spectroscopy (IR) and differential scanning calorimetry (DSC).

An increase in heating temperature and oxygen content were found to increase the formation of:

low molecular weight material
long chain branches
carbonyl, ether, and olefinic groups
conjugated sequences
insoluble material.

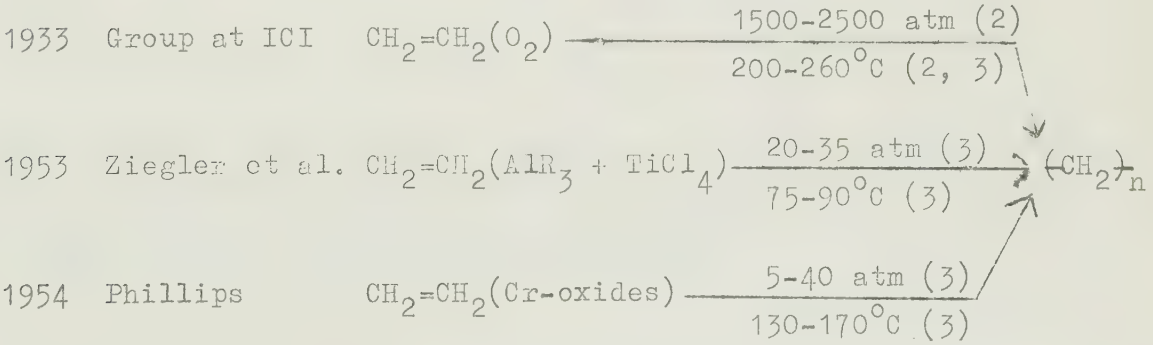
Chain scission accounts for the formation of low molecular weight material and volatiles. Molecular enlargement accounts for the formation of high molecular weight material, LCB, and ultimately the formation of insoluble material. Reaction schemes for both thermal and thermo-oxidative degradation are discussed. Initiation is suggested to be accomplished by scission of allylic C-C-bonds. Propagation is suggested to proceed by both intra- and intermolecular hydrogen abstraction, by alkyl radicals in thermal degradation, and by peroxy radicals in the thermo-oxidative degradation. Termination may occur by both combination and disproportionation. Combination reactions of alkyl radicals are suggested to account for the observed formation of LCB and high molecular weight material.

INTRODUCTION

Polyethylene (PE) is today the most used polymer in the world and accounts for about one forth (23 % in 1970) of the total production of synthetic polymers (1). Different qualities with widely different properties and end uses are produced. Plastic bags and cable insulation are typical uses for low-density polyethylene (LDPE). High-density polyethylene (HDPE) is commonly used in containers, crates and pipes to mention a few examples. The estimated world production in 1973 is 7.8 million tons for LDPE and 2.6 million tons for HDPE (1). The estimated growth up to 1975 is 13 %/year for LDPE and 15 %/year for HDPE (1).

Unifos Kemi AB in Stenungsund is the only producer of PE in Sweden and in 1973 has a capacity of 140,000 tons for LDPE and 35,000 tons for HDPE, which is about equivalent to the Swedish consumption (1).

Table 1 Some industrially important discoveries on the polymerization of ethylene



The main industrial processes used today for the production of PE (Table 1) are all the results of accidental discoveries. The first of these occurred only forty years ago at ICI in England. When R.O. Gibson in 1933 (4) attempted to react ethylene and benzaldehyde at 270°C and 1400 atm the walls of the reaction vessel were found to be coated with a film of a white waxy solid that was recognized as a polymer of ethylene. When the experiment was repeated with ethylene alone the ethylene "decomposed with great violence" to give hydrogen, methane and amorphous carbon. The decomposition caused a rapid rise in pressure and the apparatus was destroyed. In 1935, new equipment had been constructed and further experiemental work began. Due to a leak, a suitable amount of oxygen was present to initiate polymerization and 8 g of PE was obtained.

Due to the absence of polar groups, the material had interesting electrical insulating properties, especially at the high frequencies used in submarine cables. In 1939, the first plant with a capacity of a few hundred tons per year was started. During World War II a great need for flexible high frequency cables for use in radar equipment developed. The production capacity was therefore rapidly expanded in England and after 1941 even in the USA by Du Pont and Union Carbide who obtained "know how" from ICI. PE produced by this type of process is usually called "high pressure polyethylene".

When working with the synthesis and properties of organo-metallic compounds, Karl Ziegler and co-workers at the Max Planck Institut für Kohlenforschung at Mülheim/Ruhr in West Germany (5) accidentally found that ethylene could be polymerized almost at atmospheric pressure and at low temperature. The importance of the discovery was immediately recognized and by 1955 the new process was commercialized.

At about the same time, work originally directed at turning ethylene into motor fuels and synthetic lubricants by the use of chromium oxides was carried out at Phillips Petroleum Company in the USA (6). Again an accidental discovery led to a commercial process for PE. Even in this case relatively low pressures are used.

Thus, the PE produced by both the Ziegler and Phillips processes are termed "low-pressure PE". Many modifications of these processes with respect both to catalysts and reaction conditions have been made and there has even been a vapor phase process in operation since 1972 at Unifos Kemi AB (3).

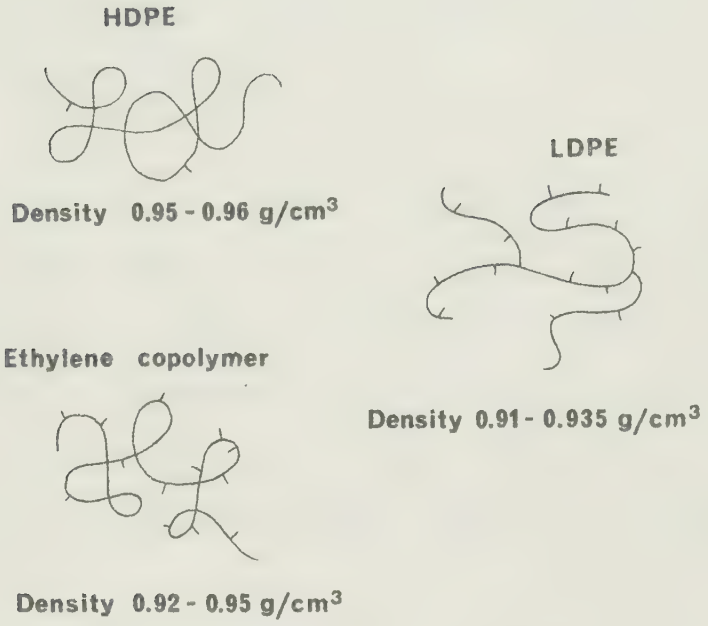


Figure 1 Schematic representation of different PE-types.

In Fig 1 the principal differences between PE produced by the different processes are illustrated.

Low-pressure processes give practically unbranched polymer chains with good close-packing ability and a crystallinity of 70-90 % (7, 8). As a result, the material is relatively stiff and has a fairly high density, 0.95-0.96 g/cm^3. It is called "high-density polyethylene" (HDPE).

In low-pressure processes ethylene may also be co-polymerized with various amounts of other 1-olefins, e.g. propene, 1-butene, and 1-hexene. The introduction of short chain branches (SCB)

as methyl, ethyl, or butyl groups disturbs the close-packing ability and a more flexible material with lower density (down to 0.92 g/cm^3) may be obtained.

High-pressure processes give PE that usually contains 20-30 SCB/1000 carbon atoms (1000 C) and in addition a few long chain branches (LCB) per 1000 C. Such branches are of a size comparable to that of the main chains. The crystallinity is 40-50 % and the densities are in the range 0.91-0.935 g/cm^3 (7). These materials are called "low-density polyethylene" (LDPE).

The branching points are assumed to be trifunctional. Besides these tertiary carbon atoms small amounts of unsaturated groups are present in PE. Typical values are given in Table 2 (7, 9, 10).

Table 2 Typical amounts of unsaturated groups per 1000 C

PE-type	Vinyl $RCH=CH_2$	Trans-vinylene $R-CH=CH-R'$	Vinylidene $RR'C=CH_2$	Carbonyl $RR'C=O$
LDPE	0.1	0.1	0.3-0.7	0.03-0.05
Phillips HDPE	0.5-2	0.1	0.1	-
Ziegler HDPE original type	0.4	0.1-0.3	0.3	-
Ziegler HDPE present type	0.1	0.1	0.1	-

The PE manufacturers deliver the material in granular form. It is then worked into various types of finished goods by the processing industry. During processing, PE is exposed to heat and mechanical forces and also to oxygen. This results in structural changes which may influence both the processability and the end use properties. The study of structural changes under processing conditions is one of the main projects at The Polymer Group at Chalmers University of Technology and the University of Gothenburg. In this thesis the results obtained when LDPE is exposed to thermal and thermo-oxidative effects are reported.

The first paper in the thesis (paper I) is an extension of a paper presented at the 8th International Gel Permeation and Liquid Chromatography Seminar in Prague, 1970 (11). It should be looked upon as the result of a preliminary study with special emphasis on the information which may be obtained by gel chromatography (GPC). This work provided the basis for the investigations reported in papers II and III, where considerable improvements and extensions have been made both in the characterization techniques and the interpretation of the data.

In common chemical practice "degradation" refers to fragmentation of the original chemical structure. In polymer chemistry the term "degradation" is applied to all structural changes which influence the polymer properties in an undesired direction (12).

POLYMER CHARACTERIZATION

Gel Chromatography (GPC)

> There is an essential difference between a simple and uniform material and a high molecular weight substance, the neglect of which prevented application of the molecule concept. All molecules have the same size in simple uniform compounds. On the contrary, high molecular compounds are mixtures of molecules of similar structure but different size. A separation into uniform products is not possible due to the small differences in their physical and chemical properties. If a molecular weight for high polymers is given, it can only be an average value.
>
> H. Staudinger, August, 1926 (13)

Gel chromatography (GPC) has been used in combination with intrinsic viscosity ($[\eta]$) to obtain MWD, molecular weight averages, and degree of LCB.

General Description and Development

Gel chromatography is a liquid chromatographic method which separates molecules according to size. A sample of a dilute polymer solution is introduced into a solvent stream which

flows through a column. The column is filled with some type of porous material ("gel") with pores of the same order of size as the dissolved molecules. As the dissolved polymer molecules flow past the "gel" they can diffuse into the internal pore structure to an extent depending on their size in solution (hydrodynamic volume (14)) and the pore-size distribution of the "gel". Larger molecules can enter only a small fraction of the internal portion of the"gel"or are completely excluded; smaller polymer molecules penetrate a larger fraction of the interior of the "gel". As the larger molecule spends less time inside the "gel" than the smaller one it will pass through to column more rapidly. The molecules are thus eluted from the column in order of their molecular size in solution, the largest being eluted first.

Although some work had been done before, it was not until J. Porath and P Flodin developed and exploited gel chromatography (or "gel filtration") that it became known to the general scientific world as an outstanding procedure to separate molecules in solution according to size. In their first paper (15) which appeared in 1959 they described cross-linked dextran gels which served as separation matrix and also the separation of a mixture of glucose and two fractions of dextran. In a series of papers from the same group in Uppsala it was also shown that e.g. polysaccharides (16), polypeptides (17), and proteins (17, 18) could be separated with the aid of gel chromatography. The dextran gels soon became commercially

available through Pharmacia AB, Uppsala under the trade name "Sephadex". Some 4800 scientific papers had appeared up to 1973 reporting the use of Sephadex for example to separate, isolate, and purify biological materials. However, Sephadex can only be used in aqueous systems and therefore most synthetic polymers cannot be analyzed.

The break-through for synthetic polymers came with the synthesis of highly cross-linked polystyrene gels that were at the same time highly porous. This development is attributed to J.C. Moore at the Dow Chemical Company, USA in 1962 and was published 1964 (19). In this paper Moore also suggested that the term "gel permeation chromatography" (GPC) should be used.Moore also designed an analytical instrument and it was rapidly built and commercialized by Water Associates Inc, USA, in 1964 (20). Several extensive general reviews on GPC have appeared, see e.g. references (21-27)

Today GPC has completely outdated the classical methods for polymer fractionation. It combines rapidity and reproduciability in a highly automatic system. About six samples can be run a day and with computer facilities the interpretation takes less than one hour. This is to be compared with about 2-3 weeks per sample for classical methods as preciptation fractionation and subsequent analysis of the fractions (28).

Experimental Conditions

The GPC-analyses reported in papers I-III have been carried out on a Waters Associates GPC 200. The GPC is equipped with an automatic injection system, a dual-headed pump, two separate lines for sample and reference flow and an all stainless steel solvent system. All sample solutions were filtered before injection and all injections (2 ml) were made by the automatic injection system. 1,2,4-Trichlorobenzene (TCB) at 135°C has been used as a solvent. Five columns in series with different pore sizes ranging from 10^3 to 10^7 Å nominal pore size giving a good separation in the molecular weight range of interest, have been used. The plate count has exceeded 3500 theoretical plates/m. Flow rate has been 1.0 ml/min and sample concentrations in the range 1-4 g/l. Usually GPC determinations have been duplicated and the chromatogram with the smallest base line drift and most well-defined start and end points has been evaluated.

Interpretation of GPC-Data

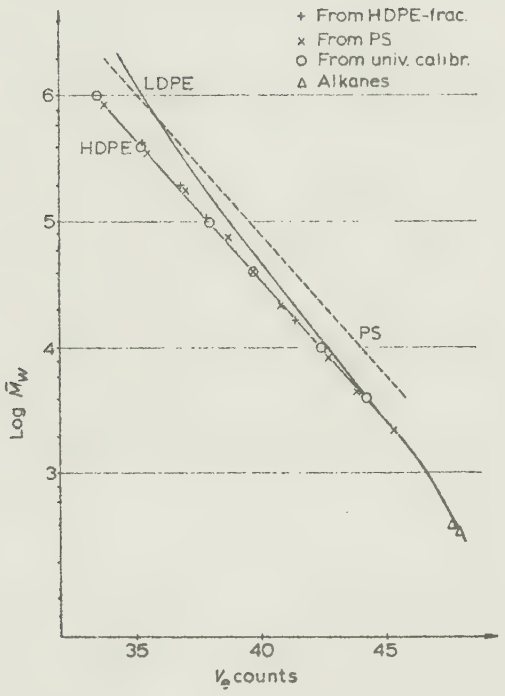


Figure 2. Calibration curves for GPC.

Since GPC is not an absolute method it has to be calibrated in order to allow a transformation of the GPC-curve into a measure of the MWD. An example of GPC calibration curves is given in Fig 2 where log M is plotted against elution volume (V_e) expressed in "counts" (5 ml eluate). Ideally GPC should be calibrated by the aid of well-characterized narrow fractions of the actual material under investigation. In practice, well-characterized narrow fractions covering the molecular weight range usually present in polymer samples are only commercially available for one polymer, linear polystyrene (PS). This fact initiated a

great deal of work in order to find a way to utilize these PS-standards to obtain the calibration curves for other polymers. In 1966 Benoit and co-workers (14, 29) suggested that the hydrodynamic volume was the key parameter in the separation process. A single "universal calibration curve" could be obtained if log $[\eta]\cdot M$ (the logarithm of intrinsic viscosity times molecular weight (M)) was plotted against elution volume. This was shown to be the case for a variety of linear and branched vinyl polymers. By using well--characterized narrow fractions other workers (30, 31) soon confirmed the validity of the "universal calibration" for PE in TCB also.

If an universal calibration curve has been established and if the relation between molecular weight and $[\eta]$ is known for a polymer, one can easily calculate the relation between molecular weight and elution volume and thus transform the GPC-curve into a MWD (32). However, the relation between molecular weight and $[\eta]$ is seldom accurately known for the whole molecular weight range of any polymer.

For HDPE the situation is relatively favourable since a Kuhn-Mark-Houwink relation, $[\eta] = K\cdot\bar{M}_w^{\alpha}$, is applicable. There is, however, some disagreement about the numerical values of K and α for TCB at 135°C, see Table 3.

Table 3 K and α values suggested for HDPE in TCB at 135°C

K	α	
$5.23 \cdot 10^{-4}$	0.70	Crouzet et al. (33)
$1.69 \cdot 10^{-3}$	0.591	Panaris and Prechner (31)
$4.6 \cdot 10^{-4}$	0.725	Drott and Mendelson (34)

The "IUPAC Working Party on Polyethylene", led by Professor Benoit, is at present attempting to overcome such discrepancies and to obtain a better agreement between results obtained in different laboratories using GPC, light scattering, and osmometry.

In our work we have used $K = 5.23 \cdot 10^{-4}$ and $\alpha = 0.70$ given by Crouzet et al. (33) to obtain the calibration curve for HDPE (Fig 2). This has been complemented with measurements on four HDPE standards with $\bar{M}_w$ from $16 \cdot 10^3$ to $420 \cdot 10^3$ available from Phillips Chemical Company. For illustrations and further details about the construction of the calibration curve for HDPE see paper I.

The two HDPE resins used in the latest IUPAC characterization round on polymers (35) were analyzed and the results are reported in paper II:

IUPAC HDPE BMWD: $\bar{M}_w = 141 \cdot 10^3$, $\bar{M}_n = 12.2 \cdot 10^3$

IUPAC HDPE NMWD: $\bar{M}_w = 60 \cdot 10^3$, $\bar{M}_n = 19.2 \cdot 10^3$

These values are in good agreement with the average values obtained by light scattering (LS) and osmometry.

Due to the presence of LCB in LDPE it is a difficult task to transform GPC-data into a MWD. As shown by Zimm and Stockmayer (36), the hydrodynamic volume of a long chain branched molecule is smaller than that of a linear one with the same molecular weight. The reduction is a function of the number of LCB per molecule. Since the molecules are separated according to hydrodynamic volume in GPC, the elution volume for long chain branched molecules will be a function of both molecular weight and extent of LCB. Since almost every sample of LDPE has different degrees of LCB a new calibration curve should ideally be constructed for every sample of LDPE. In paper I only one "average" calibration curve for LDPE is given, however. It was constructed in order to give the MWD:s and molecular weight averages the correct order of magnitude.

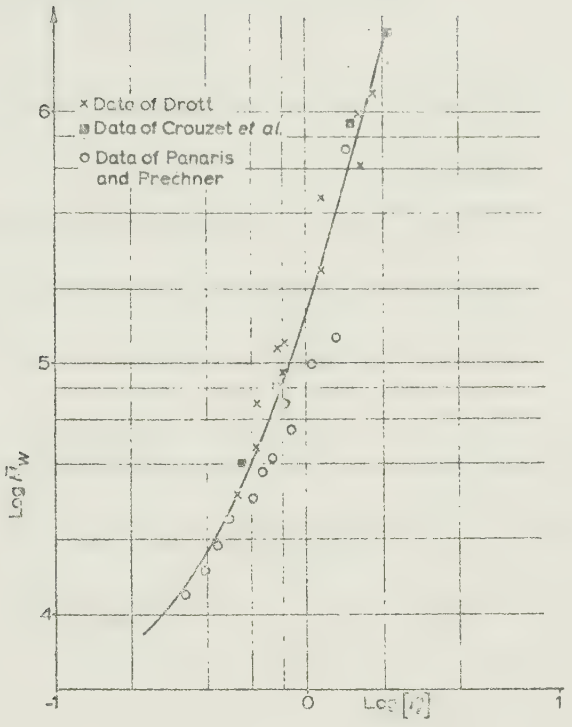


Figure 3. "Average" relationship between log [η] and log $\bar{M}_w$ for LDPE in TCB at 135°C.

Viscosity and LS measurements have been published on fractions of widely different LDPE by three different groups (31, 33, 34). These data were used to construct an "average" relation between weight average molecular weight and [η], Fig 3, which could be utilized to give a LDPE-calibration (Fig 2) via the universal calibration. MWD and molecular weight averages were calculated with the aid of Drott's computer program (37). Since the subroutines necessary for the determination of LCB were not available at this time, no measure of, or correction for, the extent of LCB could be carried out. However, in papers II and III full use could be made of the computer program.

Calculation of LCB by Drott's Method

In his method, Drott (37) combines the results of Zimm and Stockmayer (36) as to how the hydrodynamic volume of a molecule in solution changes when the extent of LCB is varied and Benoit's (29) finding that an universal calibration curve can be established for GPC.

In 1949 Zimm and Stockmayer (36) could theoretically show that if they defined g as the quotient R_{br}^2/R_l^2, where R is the radius of gyration and br and l refer to branched and linear molecules respectively, they could relate g to some average number of LCB points per molecule, n. For a polydisperse sample of comb-shaped molecules with trifunctional branch points they found that

$$\langle g_3 \rangle_w = f(n_w) \qquad (X1)$$

where n_w is the weight average number of trifunctional branch points per molecule. The best way would be to determine R^2 by LS and thereby both g and n_w. In practice it is almost impossible to reach the precision necessary to determine R^2 by LS. Since $[\eta]$ is much easier to measure and is proportional to R^3, they instead suggested that the relation

$$[\eta]_{br}/[\eta]_l = g^{\epsilon} \qquad (X2)$$

should be used. For a comb-shaped molecule ϵ should be equal to 1.5. In 1959 Zimm and Kilb (38) suggested that for star-shaped molecules ϵ should be 0.5. Drott assumed the degree of LCB (λ) to be constant throughout the molecular weight range

($\lambda = n_w/M$). With the aid of (X1) and (X2) and knowing K and α in the Kuhn-Mark-Houwink-relation he was then able to express $[\eta]_{br}$ at a certain elution volume (V_{e_i}) as a function of λ and molecular weight only.

$$[\eta]_{br_i} = [\eta]_{1_i} \cdot g^c = K \cdot M_i^\alpha \cdot [f(n_w)]^c = K \cdot M_i^\alpha \cdot [f(\lambda \cdot M_i)]^c \qquad (X3)$$

He also introduced a correction for the influence of SCB, using an expression developed by Stockmayer (39). The correction for SCB is very small. (X3) then becomes

$$[\eta]_{br_i} = K \cdot M_i^\alpha \cdot [f(\lambda \cdot M_i, \text{ SCB})]^c \qquad (X4)$$

By inserting h_i as a normalized height (proportional to the weight fraction) in the GPC-chromatogram and by summing over all V_{e_i} he obtained.

$$[\eta]_{br} = \Sigma h_i \cdot [\eta]_{br_i} = K \cdot \Sigma h_i \cdot M_i^\alpha [f(\lambda \cdot M_i, \text{ SCB})]^\epsilon \qquad (X5)$$

Beginning with a suggested value of λ and the calibration curve for HDPE the computer program compares the calculated $[\eta]$ ($[\eta]_{cal}$) with the measured one, $[\eta]_{br}$. If $[\eta]_{br}$ is lower than $[\eta]_{cal}$, λ is increased by a certain amount. Then $[\eta]_{br}$ is calculated according to (X3) for different M_i with the aid of the universal calibration according to which

$$[\eta]_{br_i} \cdot M_{br_i} = [\eta]_{1_i} \cdot M_{1_i} \qquad \text{at } V_{e_i} \qquad (X6)$$

M_{br_i} and V_{e_i} can be related giving a new calibration curve. λ is then iterated until $[\eta]_{cal} - [\eta]_{br} = 0$. The method has thus provided both a measure of the degree of LCB and a correction of the MWD and molecular weight averages. This method has been used in papers II and III.

When using this method one has to make some considerations.

1. Which values of K and α should be chosen in this connection? As discussed above, several different values have been proposed and it is difficult to favour one over the other. We have used $K = 5.23 \cdot 10^{-4}$ and $\alpha = 0.70$ given by Crouzet (33).

2. What exponent should be used for g in (X2)? Drott has used $\varepsilon = 0.5$. This choice may be questioned. However, Drott used narrow fractions of one LDPE-sample characterized by LS to calibrate the GPC. With the exponent 0.5 he found good agreement between the calculated and experimental calibration curve. An exponent value of 1.5 gave large deviations. Based on measurements on narrow LDPE fractions with LS and viscometry, exponent values of 1.0 ± 0.3 (40) and 1.3 (41) have recently been suggested. These values, however, were not used to make up calibration curves in GPC that could be compared with experimental ones.

It is reasonable to believe that there is no single value for the exponent. The relation between g and $[\eta]_{br}/[\eta]_1$ might be much more complicated varying, e.g. with molecular weight and the structure of the branches.

However, 0.5 seems to be the value of choice among almost all workers in the field (42). This is due to the fact that at the low degrees of LCB often encountered there is approximately one LCB per molecule and in that case the molecule can be considered as a three membered "star".

At this point it may be appropriate to stress that the choice of the above-mentioned values influences the absolute numerical values calculated for M/D, molecular weight averages, and degree of LCB only. If samples are compared, the relative values are independent of the choice of values for K, α, and ϵ.

Recent Developments

The assumption that λ is constant throughout the molecular weight range should also be taken into consideration. By the use of preparative GPC Otocka et al. (43) could fractionate three differently prepared LDPE-samples into 20 fractions each which were then analyzed by GPC and viscometry according to Drott's method. They found that two of the LDPE-samples had a constant degree of LCB irrespective of molecular weight while for the third sample the degree of LCB decreased with increasing molecular weight. Two other papers (40, 44) on the same subject were also published at about the same time and their results were essentially the same. Ideally then, every LDPE-sample should be fractionated and the fractions analyzed to ensure that λ is constant before the sample is evaluated by Drott's method. In

practice this is impossible. Great efforts are therefore made in many different laboratories to solve this problem through another approach. If a universal calibration curve has been established (cf. (X6)) and if either M_{br_i} or $[\eta]_{br_i}$ can be measured for the GPC-effluent, the other quantity can be calculated. In such a case, the degree of LCB and molecular weight could be obtained for the whole M.D. Two on-line discontinuous viscometric methods have been described (45, 46) that operate at about room temperature. The very low polymer concentrations encountered, however put great demands upon both temperature control and measurements of efflux time. In practice (47), the results obtained have been difficult to reproduce. Another type of continuous viscometric method was recently described by Ouano (48). He used the pressure drop across a capillary to monitor the viscosity of the GPC effluent. Although the accuracy is not of the order required for determination of LCB these preliminary results are promising.

In conclusion, Drott's method seems to provide the most versatile method thus far for a comparison of long chain branched samples.

Other Measurements

In addition to being the necessary supplement to GPC when Drott's method is used, measurements of $[\eta]$ also provide us with the possibility of comparing our data with previously published work on the degradation of PE.

Determinations of $[\eta]$ were carried out in Ubbelohde dilution viscometers.

Infrared spectroscopy was used in order to study the changes in chemical structure. All spectra were recorded on a Beckman Infrared Spectrophotometer, IR 9.

Changes in crystalline melting behaviour were studied with the aid of a Perkin Elmer DSC-1 Differential Scanning Calorimeter.

Weight changes were measured by thermogravimetry (TGA) and by discontinuous weighing on an analytical balance.

THERMAL DEGRADATION OF LDPE

Our ultimate aim is to study the structural changes and to elucidate the basic reactions when polyethylene is exposed to processing conditions, i.e. thermo-mechanical treatment in the presence of oxygen. In a recent survey (49) it was mentioned that temperatures up to 350°C are not exceptional during extrusion and injection moulding processes. It is not possible to separate mechanical from thermal effects in processing equipment. To overcome this problem, the work has been separated into two studies; one part concerning the thermal and thermo-oxidative degradation in the absence of shear forces and the other, the thermo-mechanical degradation under processing conditions. Our results concerning the thermal degradation of LDPE are presented here.

Previous work

Before our work was begun in 1969 with a preliminary investigation (50), remarkably little had been published concerning the changes occuring in the nonvolatile material when LDPE was heated between 200 and 400°C. A great deal of information was available, however, on weight loss and on the composition of the volatile products formed from polymethylene, HDPE, and LDPE above 375°C.

In 1949 Oakes and Richards (51) published their work in which

samples of LDPE of different $[\eta]$:s and densities were heated in vacuum at temperatures from 295 to 360°C up to 40 h. To study the changes in molecular size they measured $[\eta]$ and in some cases $\bar{M}_n$ by ebullioscopy. They also related $[\eta]$ to $\bar{M}_n$ by a Kuhn- Mark-Houwink-relation and used these $\bar{M}_n$ values to calculate the number of chain links broken. Changes in chemical structure were followed by infrared spectroscopy, hydrogen uptake, and iodine number.

They found that above ca. 290°C $[\eta]$ began to decrease, but gaseous products were "not formed in any appreciable quantity below about 370°C". The decrease in $[\eta]$ at 315°C and 360°C is characterized by an initial rapid drop followed by a slower change. At 360°C the decrease was about nine times as rapid as at 315°C.

Iodine number, hydrogen uptake, and infrared spectra all indicated that there was one olefinic double bond per molecule throughout the degradation. From the infrared spectra it was found that three types of olefinic groups are present in LDPE, namely vinyl $R\text{-}CH{=}CH_2$, vinylidene $RR'C{=}CH_2$, and transvinylene $R\text{-}CH{=}CH\text{-}R'$. Until extremely low $\bar{M}_n$ values ($\sim$ 1000) were reached, all three types of double bonds increased, but below this level only vinyl groups were formed.

Since Oakes and Richards report hexadecane to be stable up to 390°C under inert conditions and since they found that the initial rate of $[\eta]$-decrease was not maintained they concluded that some type

of "weak links" were present in LDPE leading to the observed decrease in $[\eta]$ even at 290°C. Suggested "weak links" were: "bonds adjacent to carbonyl or other oxygen-containing groups" and peroxide groups. Ranked as potential "weak links" were the bonds adjacent to branches in the main chain. They suggested that the degradation was initiated by rupture of weak bonds and then propagated by the points of branching in the polymer chain. This suggestion was based on Rice and Rice's (52) calculation that the probabilities of hydrogen abstraction from primary, secondary and tertiary carbons were in the ratio 1:3:33 at 300°C. The reaction chain should be characterized by few initiation points and long kinetic chain lengths.
They suggested the following reactions to account for the observed changes in "molecular size" ($[\eta]$) and chemical structure:

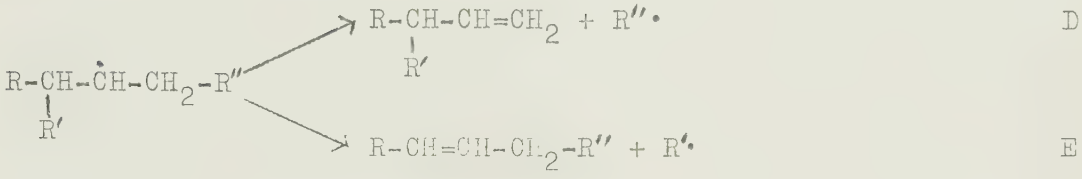
$$R''\cdot + R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R' \longrightarrow R''H + R\text{-}\dot{C}H\text{-}CH_2\text{-}CH_2\text{-}R' \qquad (A)$$

$$R\text{-}\dot{C}H\text{-}CH_2\text{-}CH_2\text{-}R' \longrightarrow R\text{-}CH{=}CH_2 + R'\text{-}CH_2\cdot \qquad (B)$$

$R\text{-}CH_2\cdot$ was then suggested to continue the reaction chain by intermolecular hydrogen abstraction.
If hydrogen were abstracted from a tertiary carbon at a branch point, then:

$$R\text{-}\underset{\displaystyle R'}{\overset{\displaystyle \cdot}{C}}\text{-}CH_2\text{-}CH_2\text{-}R'' \longrightarrow \begin{matrix} & R \\ & \diagdown \\ C{=}CH_2 & \\ \diagup & \\ R' & \end{matrix} + R''\text{-}CH_2\cdot \qquad (C)$$

If hydrogen were abstracted alpha to the branching point, then:



No termination reaction was discussed. Reactions B and D give vinyl groups, reaction C gives vinylidene groups and reaction E, trans-vinylene groups. The rapid initial drop in $[\eta]$ is consistent with the view that propagation proceeds according to random scission by <u>random</u> intermolecular hydrogen abstraction (reaction A) followed by chain scission (reactions B, C, D, and E).

If a polymer undergoes random scission the largest molecules will degrade with the greatest probability and, consequently, there will be a large decrease in average molecular weight of the nonvolatile material before any appreciable amount of volatiles have formed. Further, the MWD will rapidly approach "the most probable distribution" with a $\bar{M}_w/\bar{M}_n$ value of 2 (53). Oakes and Richards suggested that LDPE approximated this type of degradation. This view has been cited and accepted in several reviews and textbooks.

Reactions A and B were originally suggested by Wall in 1948 (54). By mass spectrometry he analyzed the volatile products from LDPE (and several other polymers) heated at 400°C in vacuum. He found

that some thirty compounds with molecular weight below 100 were formed from LDPE. They were a mixture of alkanes, alkenes, dienes, and alicyclic compounds. Ethylene was found to account for less than one per cent. He suggested a general scheme for the thermal degradation of vinyl polymers which expressed for PE has the following form.

Initiation:

$$R\text{-}CH_2\text{-}CH_2\text{-}R' \longrightarrow R\text{-}CH_2^{\bullet} + R'\text{-}CH_2^{\bullet} \qquad (F)$$

Propagation:

$$R\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\bullet} \longrightarrow R\text{-}CH_2^{\bullet} + CH_2{=}CH_2 \qquad (G)$$

$$R''^{\bullet} + R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R' \longrightarrow R''H + R\text{-}\dot{C}H\text{-}CH_2\text{-}CH_2\text{-}R' \qquad (A)$$

$$R\text{-}\dot{C}H\text{-}CH_2\text{-}CH_2\text{-}R' \longrightarrow R\text{-}CH{=}CH_2 + R'\text{-}CH_2^{\bullet} \qquad (B)$$

Termination:

$$2R^{\bullet} \longrightarrow R\text{-}R \qquad (H)$$

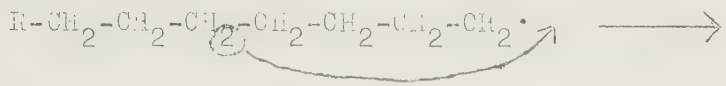
Based on his results on LDPE, Wall suggested that reaction F, followed by reactions A and B, accounted for the thermal degradation of LDPE.

In 1954 Wall and co-workers (55) summarized their work on LDPE and polymethylene heated in vacuum in the temperature range 375-400°C. They analyzed their samples by TGA and viscometry and some of the volatile products by mass spectroscopy. The quantitative determination of volatiles was restricted to alkanes and alkenes with molecular weight below 100. Propene, ethylene, 1-butene, butane, 1-pentene, and 1-hexene were the main products from polymethylene and 1-butene, butane, propane, ethane, 1-pentene, and pentane from LDPE.

For polymethylene with an extremly high molecular weight, $[\eta]^{120°C}_{p\text{-}xyl} = 20$ dl/g, they found that when 1 % volatiles had been formed $[\eta]$ had dropped to about 2 % of its initial value. It then remained approximately constant up to 15 % volatilization. Based on their results and those of Oakes and Richards (51), they proposed that reactions F, A, and B together with a termination by disproportionation are the important reactions for the thermal degradation of PE. Reaction B could also be complemented by reactions C and E if branches were present. They also pointed out that reaction A followed by reactions B, C, or E would lead to a random scission degradation of PE. Based on their results on the rate of volatilization from the TGA measurements, they concluded that polymethylene was degraded according to an almost "pure" random scission mechanism while LDPE showed some deviations caused by the presence of branches.

In his classical book on polymer degradation Grassie (56) reviewed

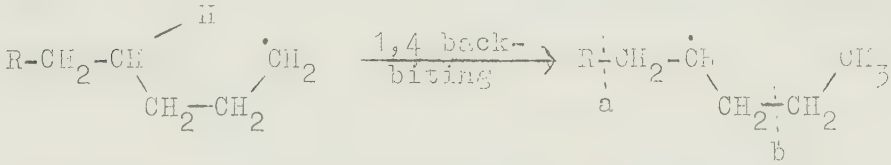
and discussed the results obtained on PE up until 1955. The interpretations and reactions presented above were supplemented, however, by an intramolecular hydrogen abstraction reaction which according to Grassie was more plausible for the formation of volatiles than reaction A.



(I)

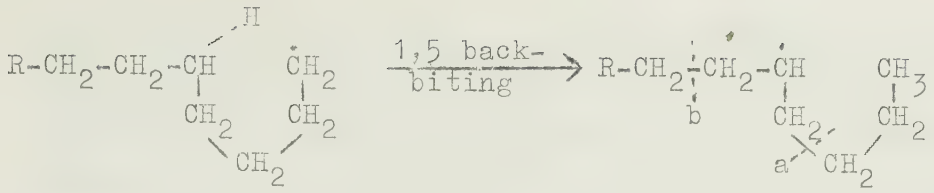
$R\text{-}CH_2^{\bullet} + CH_2{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$

Using gas chromatography for the quantitative determination of volatiles formed when HDPE and polymethylene were heated between 375 and 600°C under inert conditions. Bailey and co-workers (57, 58), van Schooten and Evenhuis (59) and Tsuchiya and Sumi (60) convincingly showed that reactions including intramolecular hydrogen abstraction and subsequent β-scission accounted for the main part of the volatile material. Analyzing up to C_5, Bailey and Liotta (57) suggested that depolymerization, reaction G, together with 1,4- and 1,5 "back-biting", reactions K and L accounted for the observed products.



(K)

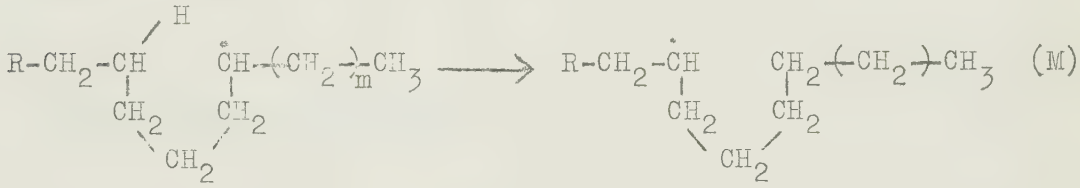
Scission at a gives an ethyl radical and at b 1-pentene.



(L)

Scission at a gives a propyl radical and at b 1-hexene. The alkyl radicals were then supposed to abstract hydrogen intermolecularly and form alkanes. Bailey and Baccei (58) could also prove this later by using HDPE mixed with polytetradeuteroethylene. Reaction L (and K) is simply a better presentation of reaction I.

Based on results from analyses up to C_{11} van Schooten and Evenhuis (59) suggested that the intramolecular reactions also could proceed further by repeated back-biting.



(M)

From analyses of the main products from polymethylene up to C_{16} and everything detectable below C_6 from HDPE, Tsuchiya and Sumi (60) could confirm the importance of the suggested mechanisms G, K, L, and M.

In the work, that essentially dealt with HDPE, Quackenbos (61) also reported the changes in $[\eta]$ of an LDPE heated at 365°C under nitrogen. The general appearance of the curve is in close agreement with the findings of Oakes and Richards (51). The heating

time scale is quite different, however. Changes that took hours in Oakes' and Richards' experiments took only minutes in Quackenbos'. According to Quackenbos this discrepancy may have arisen from problems which Oakes and Richards had with their temperature measurements and heat transfer to the sample under the vacuum conditions used. Quackenbos favoured a random scission mechanism for PE to explain his experimental results.

This Work

Since there was a general agreement, which lacked experimental confirmation, that the nonvolatile parts of LDPE are degraded by a random scission type of mechanism we decided to investigate this problem.

Preliminary Investigation

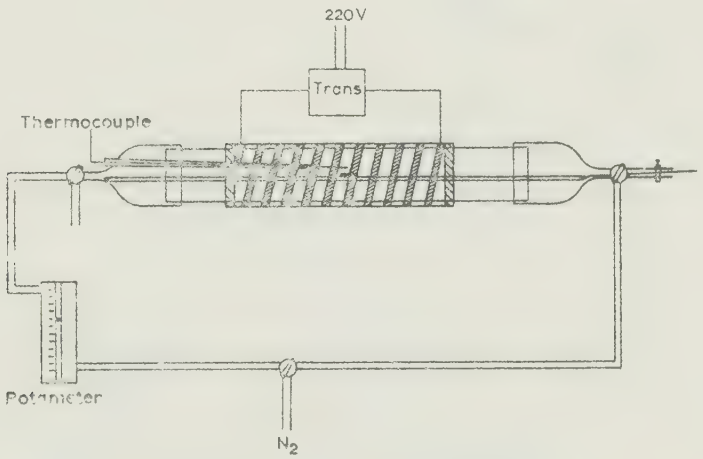


Figure 4. Tubular oven used for heat treatment.

The samples were heated as 0.3 mm thick films in a tubular oven, 1.20 m long and 0.065 m in diameter, Fig 4. The heating temperatures ranged from 284 to 355°C and heating times from 2 to 90 min. The nitrogen-oxygen mixture used and considered as "pure" nitrogen was reported to contain 0.0063 % (by volume) of oxygen (O_2). The LDPE-resin (MI = 0.24, Dens = 0.921) was kindly supplied by Unifos Kemi AB and was reported to be free from additives.

None of the samples were discoloured nor did they contain insoluble material. They became, however, more and more brittle during the heat treatment. The samples were analyzed by GPC and viscometry but no correction for LCB was made.

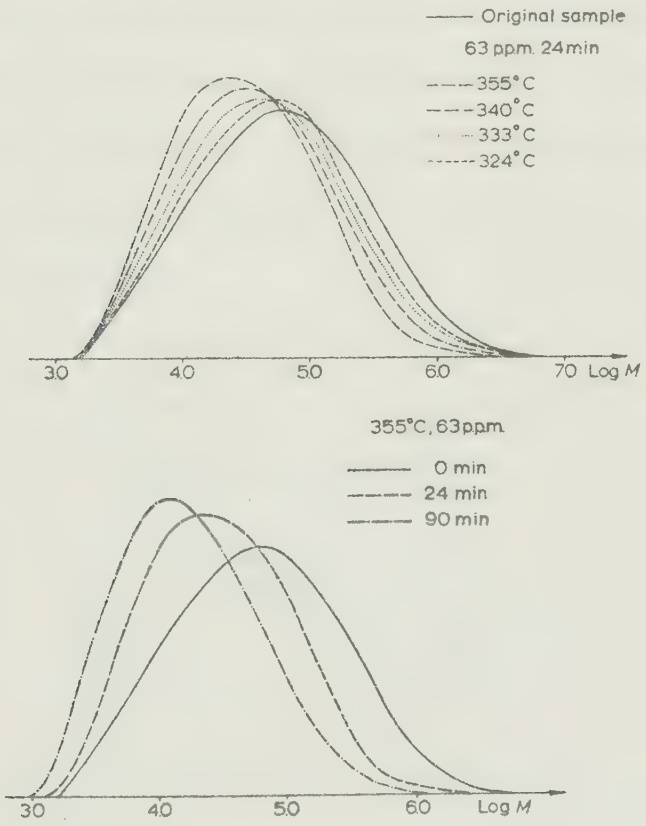


Figure 5. MWD for samples heated under 0.0063 % O_2.

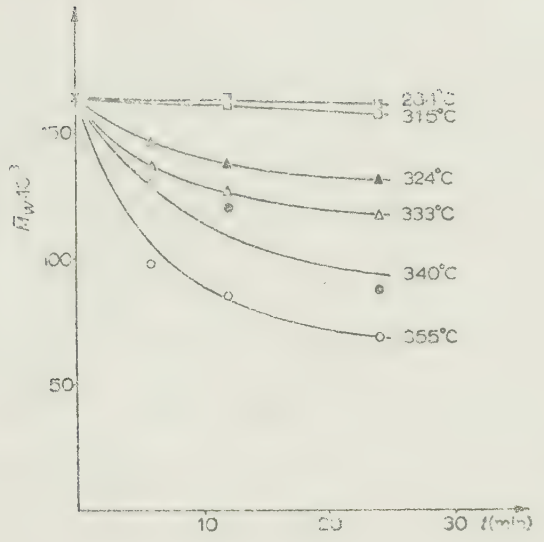


Figure 6. Change in $\bar{M}_w$ for samples heated under 0.0063 % O_2.

The results from GPC are shown in Fig 5 and 6. $\bar{M}_w/\bar{M}_n$ was almost constant in most cases, after 90 min at 355°C (the most severe treatment) it was about 5. As can be seen from Fig 5, and increase in heating time gave the same effects as an increase in heating temperature.

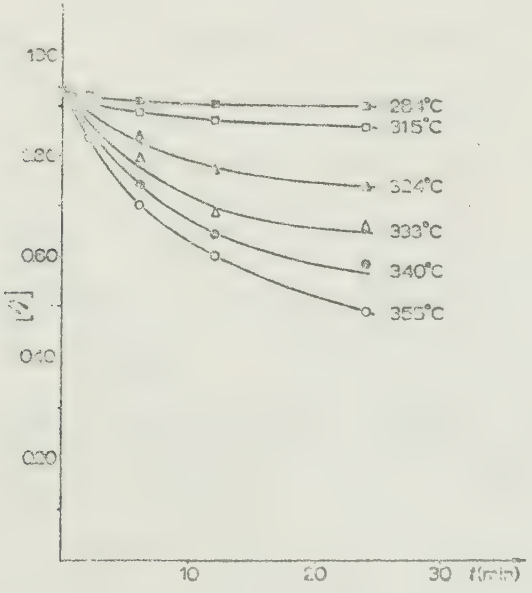


Figure 7. Change in $[\eta]$ for samples heated under 0.0063 % O_2.

The viscometric results are shown in Fig 7.

We found that the shape of the $[\eta]$- decrease was in good agreement with both Oakes and Richards (51) and Quackenbos (61) results and that the time needed to effect certain changes was in agreement with Quackenbos findings.

The results from $\bar{M}_w$- and $[\eta]$-decrease were in agreement with a behaviour expected for a polymer undergoing a random scission type of degradation according to a reaction sequence of the type suggested by Oakes and Richards (51). The changes in MWD's and $\bar{M}_w/\bar{M}_n$ were puzzling, however. The high molecular weight end of the MWD's did not vanish rapidly. On the contrary, it changed slowly and even after 90 min at 355°C material with molecular weight in the order of one million was present. Furthermore, the MWD showed no tendency to approach "the most probable distribution" with $\bar{M}_w/\bar{M}_n = 2$, although molecular weight averages had been substantially reduced. In spite of these results a random scission type of mechanism was assumed to be consistent with the observed changes in the nonvolatile material.

The formation of volatile material was assumed to be due to intramolecular hydrogen abstraction as shown e.g. by Tsuchiya and Sumi (60) for HDPE. Quackenbos (61) had suggested that the volatiles were formed by random scission of the low molecular weight parts of the MWD. Our GPC results did not confirm this suggestion since no material with molecular weight below one thousand was formed even after 90 min at 355°C (Fig 5).

The treated samples were also analyzed by IR and DSC. The results obtained were in excellent agreement with the results reported in paper II (see below).

Note: The weight loss data reported in paper I corresponded to 0.28 % O_2 and not to 0.0063 % O_2 as stated.

Main Investigation

When Drott's computer program was completely adapted to the computer available (IBM 360/65) the measurements were reinterpreted by combining GPC and viscometric data. The results were quite inconsistent with a random scission type of degradation. A new investigation was begun utilizing a new LDPE-resin and nitrogen-oxygen mixtures in order to check the reliability of our findings. The LDPE chosen was Unifos DFDS 6600 (MI = 0.31, Dens = 0.922) since it was reported to be free from additives and since it had been chosen as one of the polymers for co-operative research work carried out under the auspices of Nordforsk. Furthermore, large quantities of the same batch were available, which is essential when the thermo-mechanical degradation is studied.

The same heating procedure as described above was used. The heating temperatures ranged from 284 to 355°C and the heating times from 6 to 90 min. The high purity grade nitrogen used was reported to contain 0.00028 % (by volume) of O_2.

Changes in MWD, molecular weight averages, and degree of LCB were

followed by GPC combined with viscometry using Drott's method for the interpretation. Other structural changes were investigated by IR and DSC.

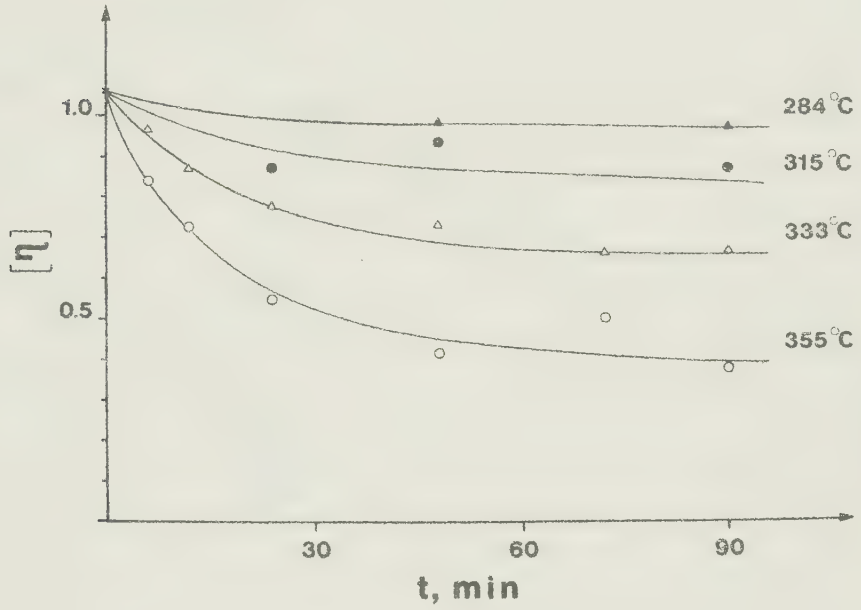
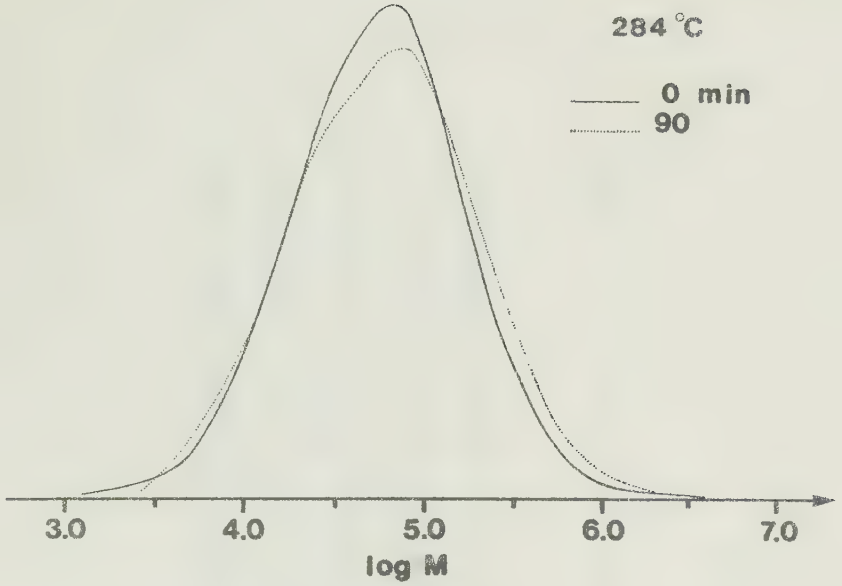


Figure 8. Change in [η] with heating time and temperature.

As in paper I none of the samples were discoloured nor did they contain insoluble material. The changes in intrinsic viscosity with time and temperature are shown in Fig 8. The relative appearance of the curves is in agreement with the findings reported in paper I. At 284°C a small decrease is observed while at 315, 333 and 355°C the decrease becomes more and more rapid.



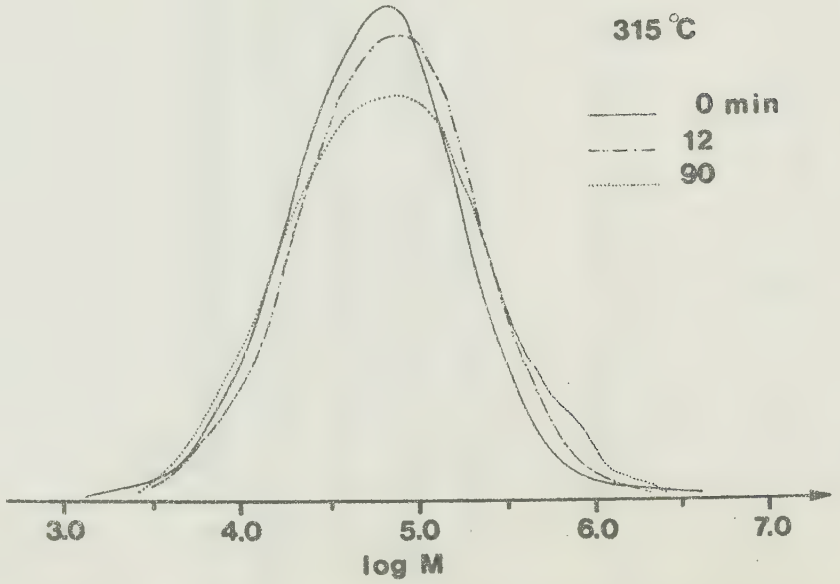
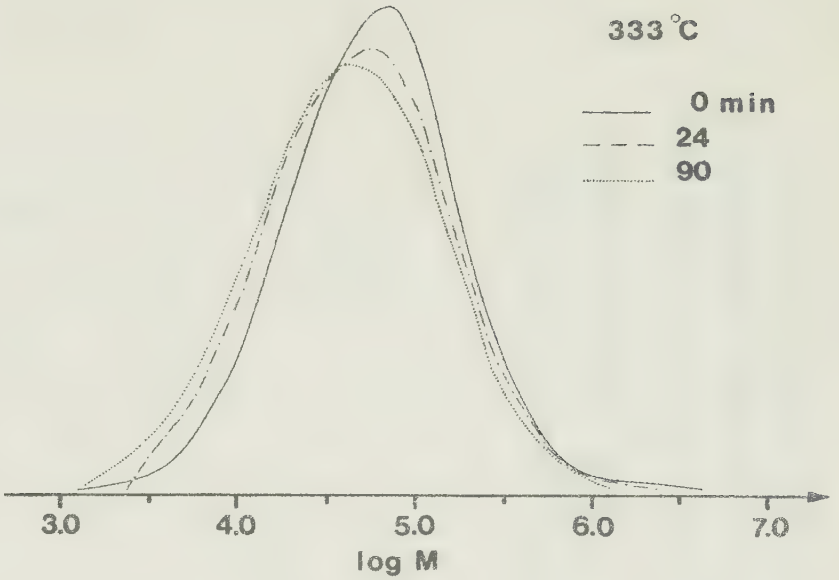


Figure 9. MWD for samples heated at 284 and 315°C



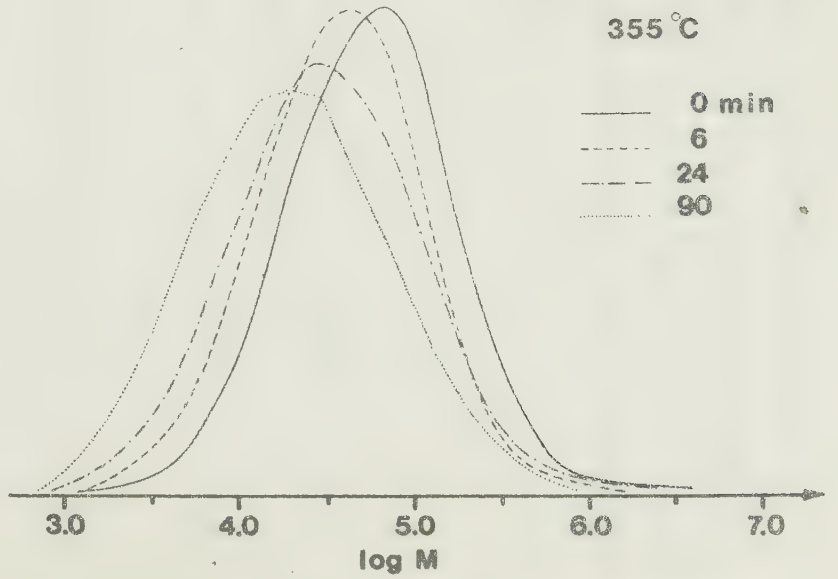


Figure 10. MWD for samples heated at 333 and 355°C

The changes in MWD, Fig 9 and 10 show, however, marked differences from the uncorrected MWD:s presented in paper I. Heating at 284 and 315°C results in a shift of the MWD towards higher molecular weight. At 333 and 355°C a shift towards lower molecular weights is observed.

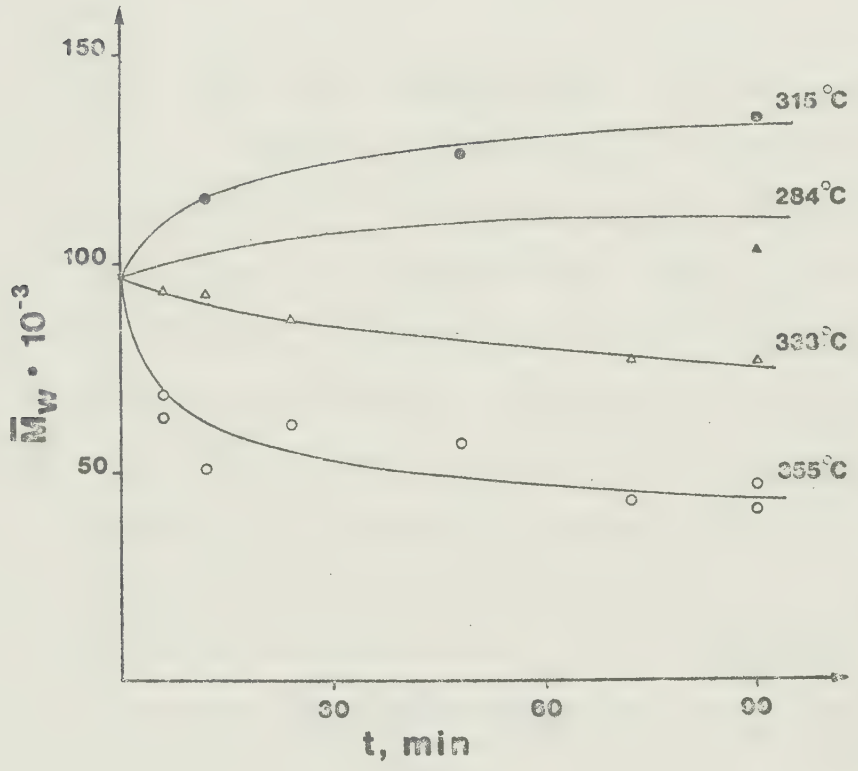


Figure 11. Changes in $\bar{M}_w$ with heating time and temperature.

The changes in MWD expressed in terms of $\bar{M}_w$ are shown in Fig 11. At 284 and 315°C $\bar{M}_w$ increases while at 333 and 355°C a decrease is observed. $\bar{M}_w/\bar{M}_n$ showed a constant value at 284°C and an increase from about 3 to about 4 after 90 min at the other temperatures. The degree of LCB also increased with heating time. The

increase is larger the higher the temperature. After 90 min λ had increased from $\sim 0.7 \cdot 10^{-4}$ to about twice that value at 284°C, $\approx 2 \cdot 10^{-4}$ at 315°C, $\approx 4 \cdot 10^{-4}$ at 333°C, to $\approx 6 \cdot 10^{-4}$ at 355°C. These remarkable results were in complete accordance with those obtained when Drott's method was used for the reinterpretation of the data obtained in the preliminary investigation.

As discussed under "gel chromatography" both $[\eta]$ and the separation in GPC is dependent on hydrodynamic volume and, consequently, both on molecular weight and extent of LCB. Although $\bar{M}_w$ increases at 284 and 315°C, $[\eta]$ decreases as the degree of LCB is simultaneously increased. At 333 and 355°C both the decrease in $\bar{M}_w$ and the increase in LCB co-operate to reduce $[\eta]$. Since the dependence of LCB on $[\eta]$ was not taken into account when the $[\eta]$-decreases was interpreted in the studies discussed above (51, 55, 61), it must be realized that their conclusions on a random scission mechanism for PE were based on undue simplifications. It is fair to speculate that the enormous $[\eta]$- decrease reported by Wall (55) for polymethylene was mainly due to increase in LCB and not to an enormous decrease in $\bar{M}_w$ as it has been interpreted (55, 62, 63).

The increase in the high molecular weight material of the MWD's at 284 and 315°C, Fig 9, can not be solely explained by the formation of larger molecules containing LCB. Other molecular enlargement reactions must also be considered.

Based mainly on the experimental results presented in paper II

and the experimental results and reactions suggested by Wall (54), Oakes and Richards (51), Grassie (56), Bailey et al. (57, 58), van Schooten (59), and Tsuchiya and Sumi (60), we have proposed the reaction scheme shown on page 42 for the purely thermal degradation of polyethylene in the temperature range 280-360°C.

Since LDPE starts to degrade at about 100°C lower than hexadecane (51), some structural "impurity" must be suspected. Since LDPE contains branch points, and olefinic and carbonyl groups (Table 2), the presence of these, together with hydroperoxide groups, have generally been put forward as such impurities. Since the presence of hydroperoxides in LDPE has never been experimentally proved, hydroperoxides were not further considered as a source of initiation. In order to check if the three other types of extraneous structures could be discriminated, we looked at the bond dissociation energies for model compounds. We found that the C-C bond in the allylic position had the lowest bond dissociation energy, 257.7 kJ/mol (61.5 kcal/mol) (64). The C-C bond in the position alpha to the carbonyl had 301.7 kJ/mol (72 kcal/mol) (65) and the C-C bond in the position alpha to a branching point had 335.2 kJ/mol (80 kcal/mol) (66).

Depolymerization, reaction 4 (reaction G) and intramolecular hydrogen abstraction (back-biting) followed by β-scission, reactions 5, 6, 7, and 8 (reactions K, L, and M) have been convincingly shown to fully account for the formation of volatile material around 400°C. Since we did not observe any material with

Initiation

1

2

3

Propagation

Depolymerization

4

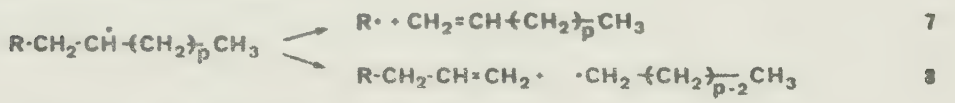
Intramolecular hydrogen abstraction

5

6

n, m = 2 or 3

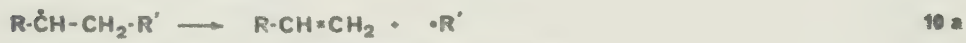
Subsequent β-scission


7 8

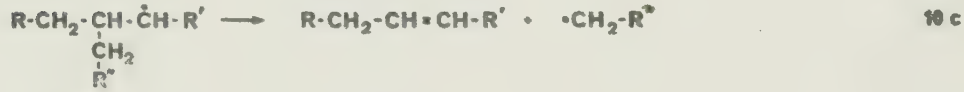
Intermolecular hydrogen abstraction

9

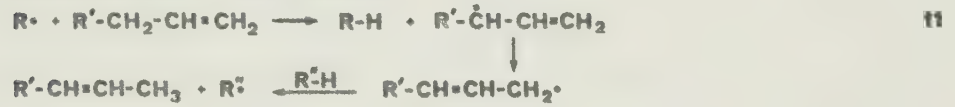
Subsequent β-scission


10 a

10 b


10 c

Isomerization of vinyl group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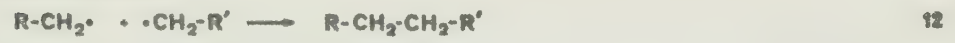
Termination

Combination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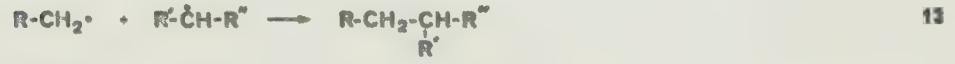
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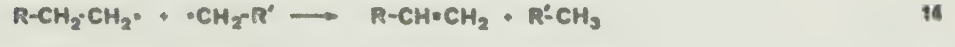
Disproportionation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15

molecular weight below 800 in the M.D's and since we had a weight loss of 1.5 % after 90 min at 355°C we assume that these suggestions are valid under our conditionas also. The weight loss was in good agreement with published data from TGA measurements (67).

Since reactions 5-8 excert only a minor influence on changes in the M.D, reactions 9 and 10 (reactions A, B, C and E) involving intermolecular hydrogen abstraction and subsequent β-scission are considered to be responsible for chain scission resulting in a large decrease in molecular weight.

Besides being responsible for the decrease in molecular weight, reactions 10 a-c were also considered to explain the observed increase (51) in vinyl, vinylidene and trans-vinylene groups. We found that the vinyl groups showed a larger increase than did the trans-vinylene and vinylidene groups. The carbonyl content was small and was further reduced during heating. Another possibility other than reaction 10 c for the formation of trans-vinylene groups is reaction 11. The abstraction of hydrogen from an allylic position should be highly favoured compared to addition of the free radical to the double bond at temperatures above 300°C.

Since both combination and disproportionation between radicals are known to occur (68, 69), termination was suggested to be accomplished by reactions 12-15. For primary radicals it has been estimated that combination is about 10 times as probable as dis-

proportionation at temperatures between 300 and 400°C (70). In reactions between primary and secondary radicals the disproportionation reaction will be more important (68, 71).

Since radical addition to olefinic groups was not considered probable under our conditions, reactions 12 and 13 are the only way in which larger and more branched molecules are formed. Since it is reasonable to assume that reaction 12 occurs more frequently than reaction 13, the combination of primary alkyl radicals is suggested to account for the main part of the molecular enlargement observed. The disproportionation reactions 14 and 15 also offer alternative ways of formation for vinyl and trans-vinylene groups.

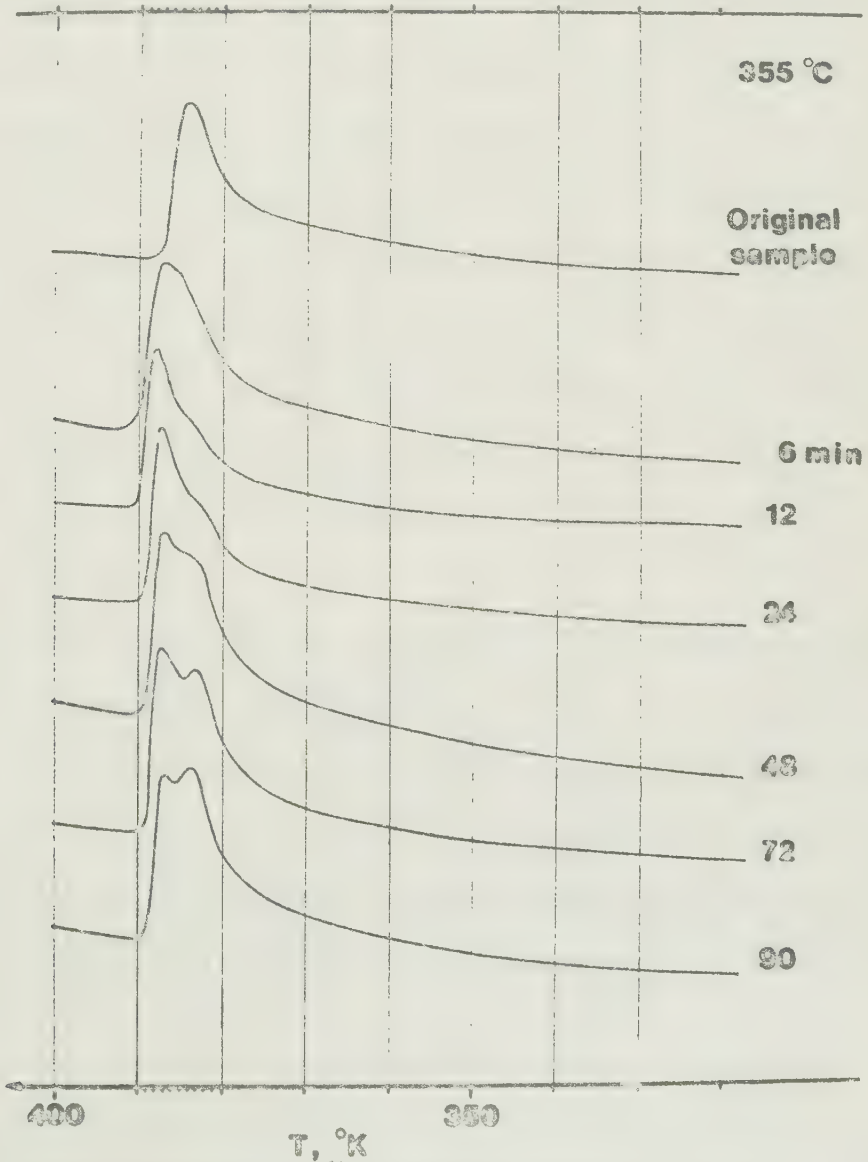


Figure 12. DSC thermograms for samples heated at 355°C.

The DSC thermograms for samples heated at 355°C are given in Fig 12. At lower temperatures no significant changes occur. One peak is developed at ~ 3°C higher temperature than the original peak. Like the density, which increased from 0.922 g/cm^3 to 0.924 g/cm^3 after 6 min and to 0.930 after 24 min of heating, the area under the curve showed a tendency to increase with heating time which indicates an increase in crystallinity. Crystallinity usually correlates well with the amount of SCB. As is usually done, the amount of SCB was determined by means of IR and expressed as CH_3/1000 C. The values obtained were corrected for methyl groups at the main chain ends. The untreated polymer is assumed to contain methyl end groups only. Chain scissions during degradation will produce an equal amount of methyl and unsaturated chain ends, however. The following correction was thus applied:

Corrected value = Uncorrected value - $14{,}000 \cdot (1/\bar{M}_{n_o} + 1/\bar{M}_n)$

where $\bar{M}_{n_o}$ is equal to $\bar{M}_n$ for the untreated sample. We found the following amounts of CH_3/1000 C: untreated sample 20, after heating 6 and 24 min at 355°C, 22.5, and after heating 90 min at 355°C, 15. Obviously there is no correlation between the area changes in the DSC thermograms and the SCB values.

We instead suggested that the increase in peak temperature and crystallinity could be explained by the fact that a considerable amount of low molecular weight material was formed simultaneously, Fig 10. These shorter, more mobile chains will have an increased probability of attaining highly ordered structures. The development of the lower melting peak in the thermogram may to some

extent be a result of the increased amount of olefinic groups and chain ends which are formed during degradation.

Conclusions

When LDPE free from additives is heated under nitrogen in the temperature range 284-355°C, the observed molecular changes are not consistent with a random scission type of degradation. Instead, both chain scission and molecular enlargement reactions occur. The latter will partly result in long chain branches, which will strongly influence the relationship between $[\eta]$ and $\bar{M}_w$. This has previously not been taken into account when the rapid drop of the intrinsic viscosity in polyethylene degradation has been interpreted. The molecular enlargement reactions are found to dominate at 284 and 315°C, while chain scission dominates at 333 and 355°C.

THERMO-OXIDATIVE DEGRADATION OF LDPE

During processing PE is not only exposed to high temperature and shear forces, but also to oxygen. Little has been published on the structural changes in PE when subjected to such conditions.

Previous work

Since Quackenbos (61) found that the oxidative attack during processing corresponded to a fairly low oxygen level, he used 0.34 % oxygen in nitrogen in his study which mainly concerned HDPE, but the results on LDPE are reported to be about the same. He heated the polymer (0.25 mm thick films) at temperatures between 150 and 400°C and measured the changes in $[\eta]$ and carbonyl content.

Quackenbos (61) found that the presence of oxygen (0.34 %) resulted in a more rapid decrease in $[\eta]$ than in pure nitrogen (0.0008 % O_2) and also in the formation of carbonyl groups and discolouration. The relative $[\eta]$-decrease was found to be larger at lower temperatures. The formation of carbonyl groups, as measured by IR on the nonvolatile material, was found to be approximately independent of heating temperature between 300 and 400°C. It was also found that at 150°C diffusion of oxygen into the sample was slow in comparison with the reaction rate.

Many papers have been published on the oxidative changes of PE

below 200°C in air or other oxygen-rich atmospheres. An excellent survey of such studies was recently published by Reich and Stivala (72).

This Work

Preliminary Investigation

In our preliminary study concerning the thermo-oxidative degradation of PE, paper I, the same LDPE resin, characterization methods, and degradation equipment as described above for the preliminary study of thermal degradation were used. The samples were treated at 355°C between 6 and 90 min. The nitrogen-oxygen mixtures used were reported by Nordiska Syrgasverken AB to contain from 0.0022 to 0.280 % (by volume) of O_2. Subsequent checks at AGA, AB have shown that the mixture stated to contain 0.041 % O_2 actually contained 0.0095 % O_2. All other mixtures were found to be correctly analysed.

MWD's, $\bar{M}_w$'s, and $[\eta]$'s gave two separate sets of degradation curves. One for the oxygen contents ≤ 0.0095 % O_2 and the other for oxygen contents between 0.100 and 0.280 % O_2. The increased rate of $[\eta]$- and $\bar{M}_w$-decrease was found to be two to four times larger at the highest oxygen levels.

The changes in the high molecular weight end of the MWD's at the highest oxygen levels were similar to those reported for 0.0063 % O_2. The decrease was somewhat more pronounced. In the low mole-

cular weight end the influence of oxygen was more marked since an appreciably larger amount of low molecular material was formed than in 0.0063 % O_2.

Like Quackenbos (61) we found that the samples treated for 90 min at the highest oxygen levels were discoloured. In the most severe case the sample acquired a thin brown surface layer.

Main Investigation

In our next study, paper III, the same LDPE resin (Unifos DFDS 6600), characterization methods, degradation procedure and heating conditions as described above for the thermal degradation reported in paper II were used. The nitrogen-oxygen mixtures were delivered by AGA, AB and reported to contain from 0.020 to 1.16 % (by volume) of O_2.

With several of the samples the surface layer was discoloured. Discolouration increased with time, temperature, and oxygen content. Heavily degraded samples were almost black and contained a minor amount of insoluble material. For example, heating for 90 min at 355°C in 0.34 % O_2 resulted in a thin brown surface layer and 2-3 % insoluble polymer. Below this layer the polymer had turned yellow. The discolouration gradually decreased with the distance from the surface. The observed formation of thin highly discoloured surface layers indicated that the attack of oxygen was reaction- and not diffusion-con-

trolled. Thus, since the treated samples were heterogeneous, the results were considered qualitative. Even a considerable reduction of sample thickness would not have ensured a homogeneously oxidized material (73).

For purposes of comparison, results obtained in high purity nitrogen (paper II) were occasionally included.

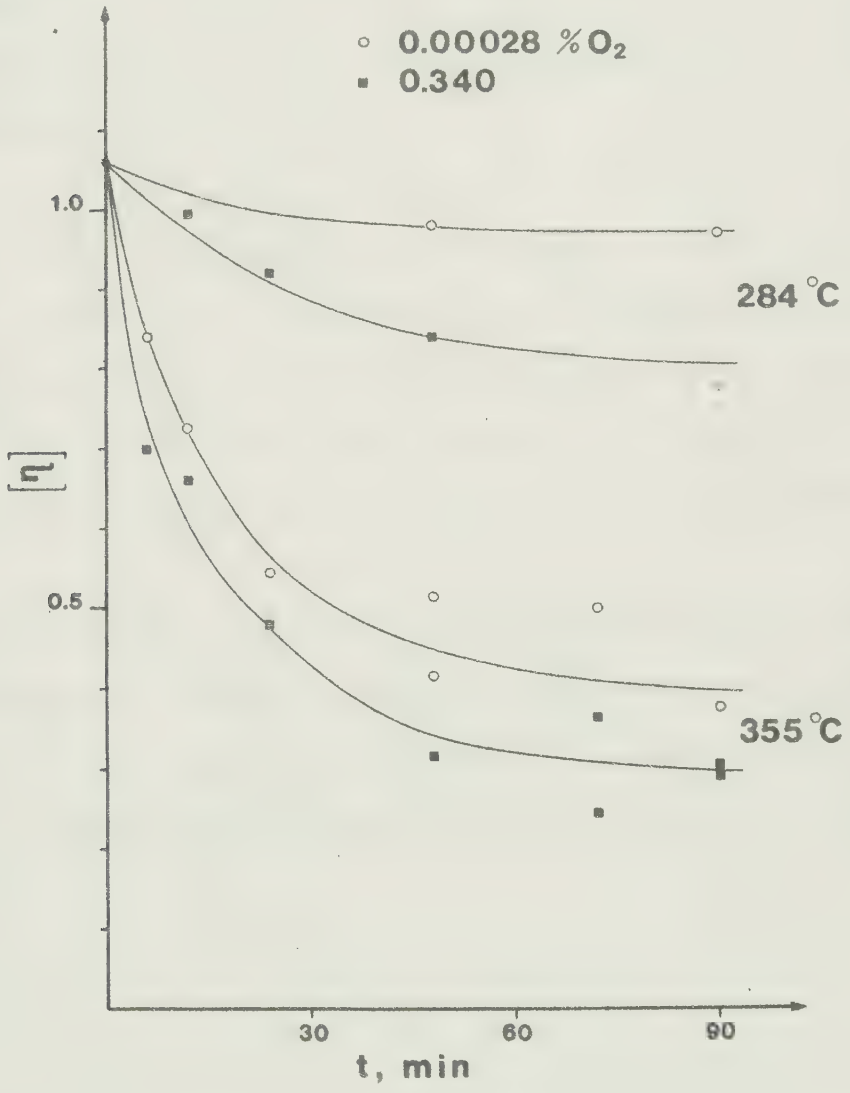


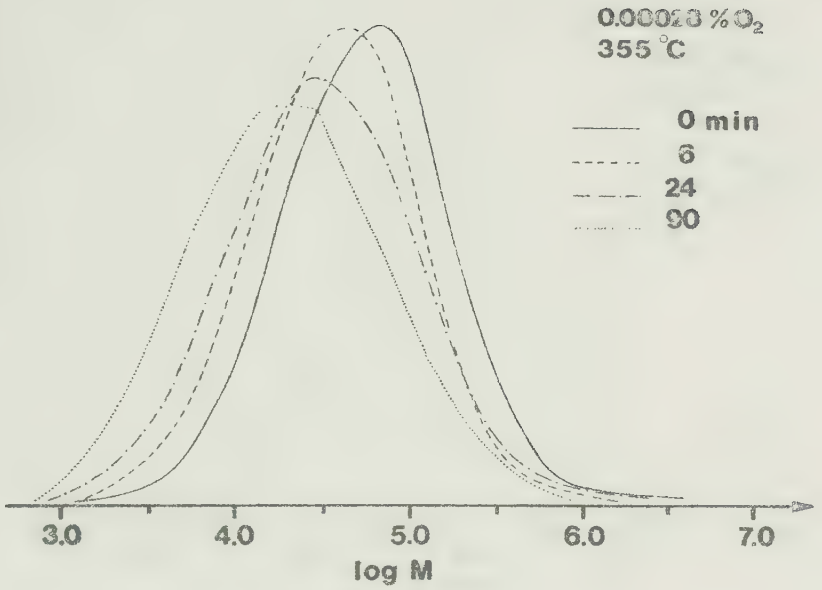
Figure 13. Change in [η] with heating time and oxygen content.

The changes in $[\eta]$ shown in Fig 13 agree with Quackenbos findings (61) that oxygen has a much larger relative effect on the decrease in $[\eta]$ at lower temperatures.

Fig 14 and 15 illustrate the effect of the oxygen content on the changes in MWD. The pronounced increase in low molecular weight material with an increase in oxygen content is easily recognized. The complex changes in the high molecular weight tail of the MWD, e.g. at 1.16 % O_2, indicate that molecular enlargement also occurs.

The effect of temperature on the changes in MWD is shown in Fig 16 and 17. As in the pure thermal degradation, the high molecular weight end increases at 284°C. At 315°C, however, a decrease is noticed. The formation of low molecular weight material is greatly enhanced by an increase in temperature.

At 284°C the $\bar{M}_w$ values increased while at 315°C a slight increase was followed by an appreciable decrease. At 355°C the $\bar{M}_w$'s showed an initial rapid drop followed by minor changes. $\bar{M}_w/\bar{M}_n$ values showed a general increase with time and oxygen content.



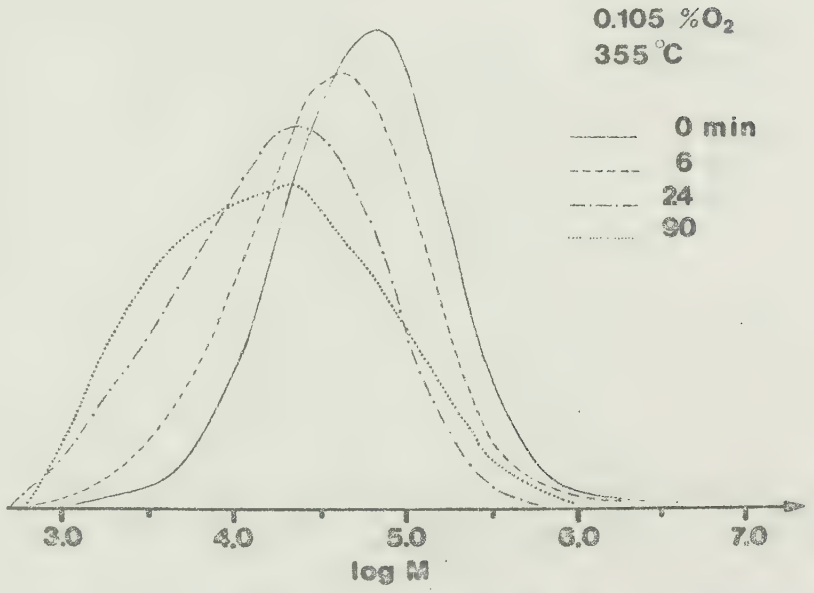
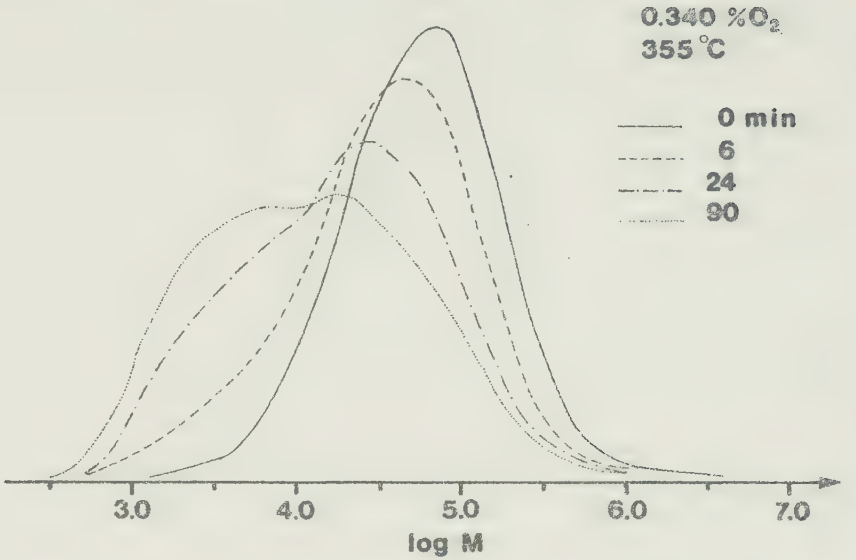


Figure 14. MWD for samples heated at 355°C in 0.00028 and 0.105 % O_2.



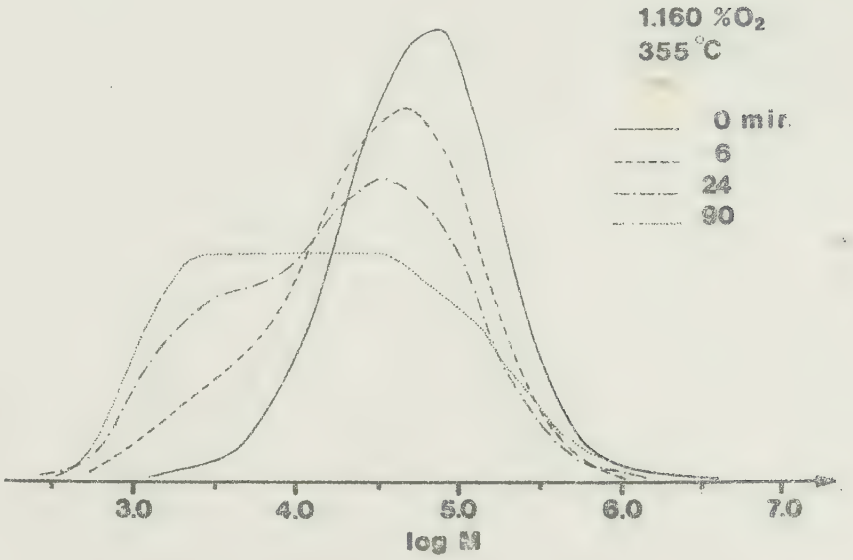
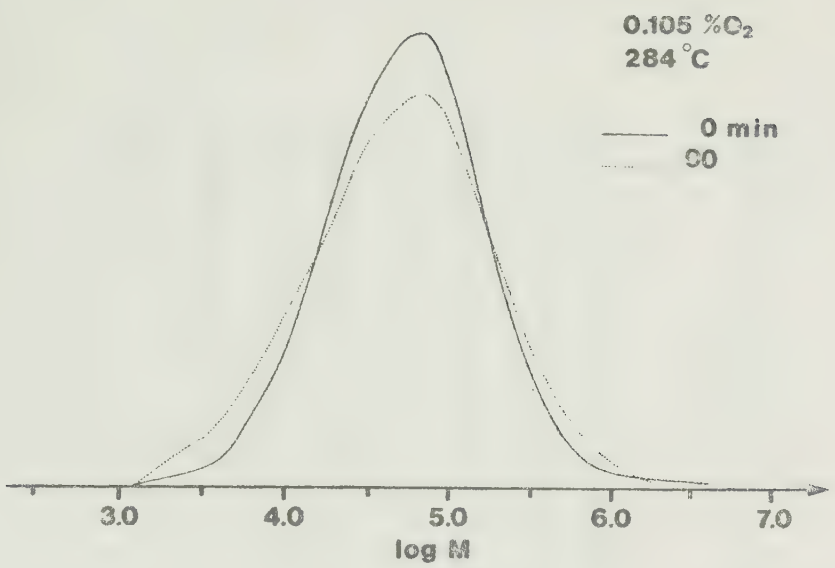


Figure 15. MWD for samples heated at 355°C in 0.340 and 1.16 % O_2.



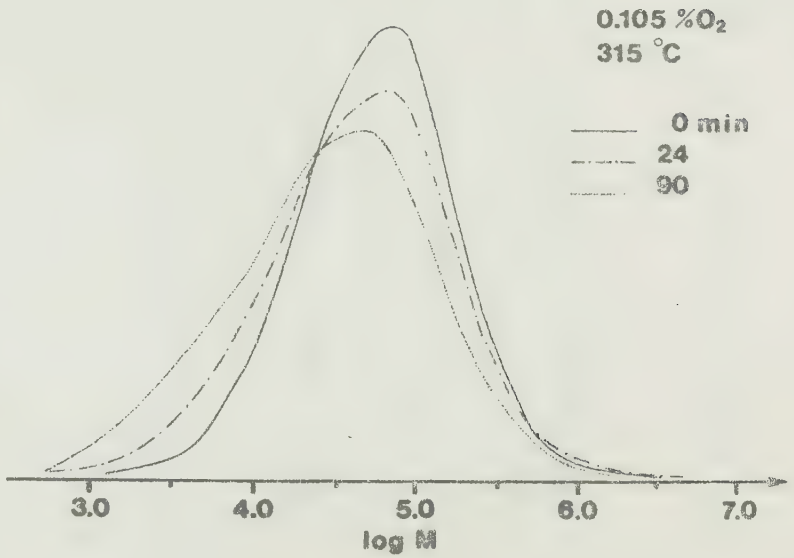
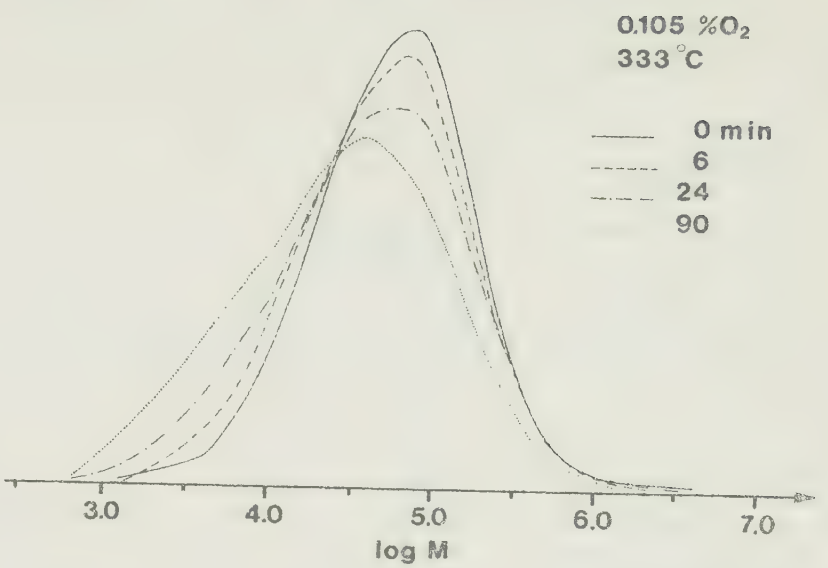


Figure 16. MWD for samples heated in 0.105 % O_2 at 284 and 315°C.



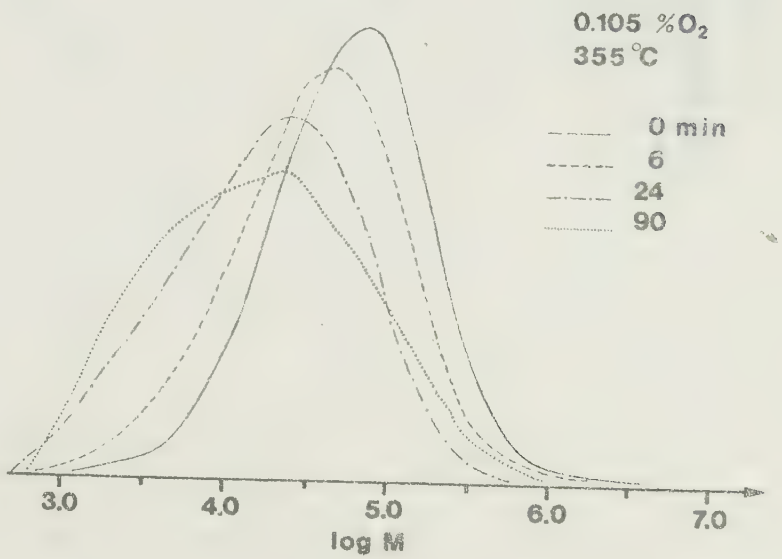


Figure 17. MWD for samples heated in 0.105 % O_2 at 333 and 355°C.

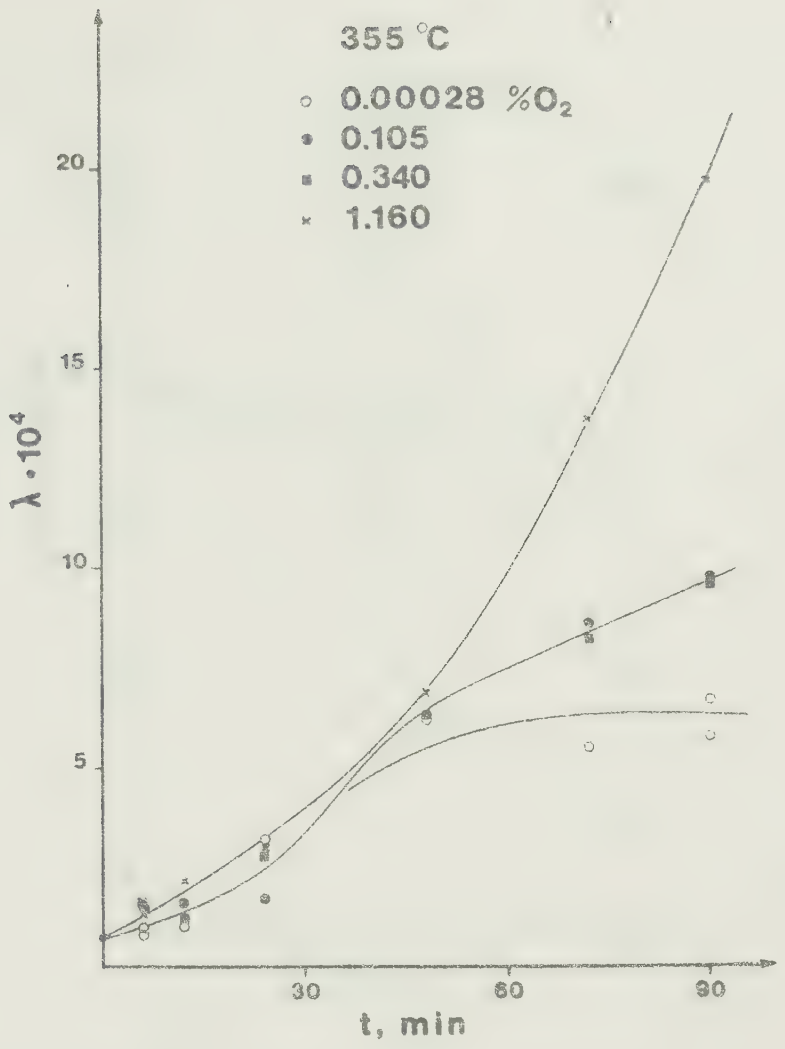


Figure 18. Change in the degree of LCB (λ) with heating time at 355°C.

As in pure thermal degradation, the degree of LCB changed. At 284 and 315°C a small increase is observed (from $0.7 \cdot 10^{-4}$ to $\sim 2 \cdot 10^{-4}$ after 90 min). At 333°C the increase passes a maximum ($\sim 4 \cdot 10^{-4}$) and after 90 min λ is in the range $2\text{-}3 \cdot 10^{-4}$. The maximum value is reached in a shorter time at higher oxygen levels (24 min of heating in 1.16 % O_2). As shown in Fig 18 no maximum value is observed at 355°C but rather a continous increase.

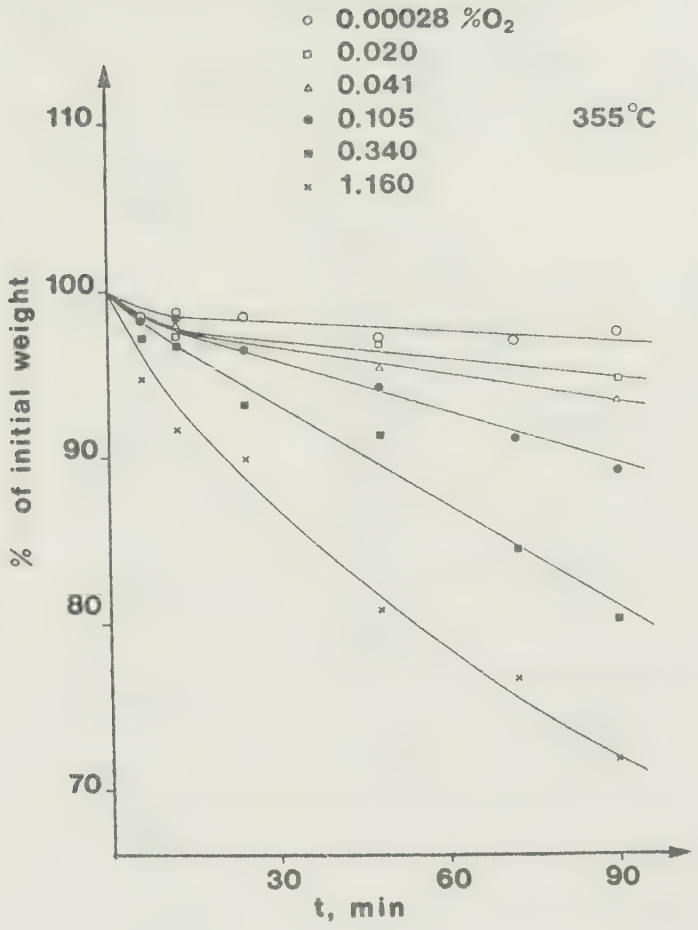


Figure 19. Weight loss at 355°C.

The pronounced influence of oxygen content on changes in sample weight is shown in Fig 19. The effect of temperature can be illustrated by the observation that after 90 min in 1.16 % O_2 the weight loss was ≈ 30 % at 355°C, ≈ 13 % at 333°C, ≈ 6 % at 315°C, and ≈ 4 % at 284°C.

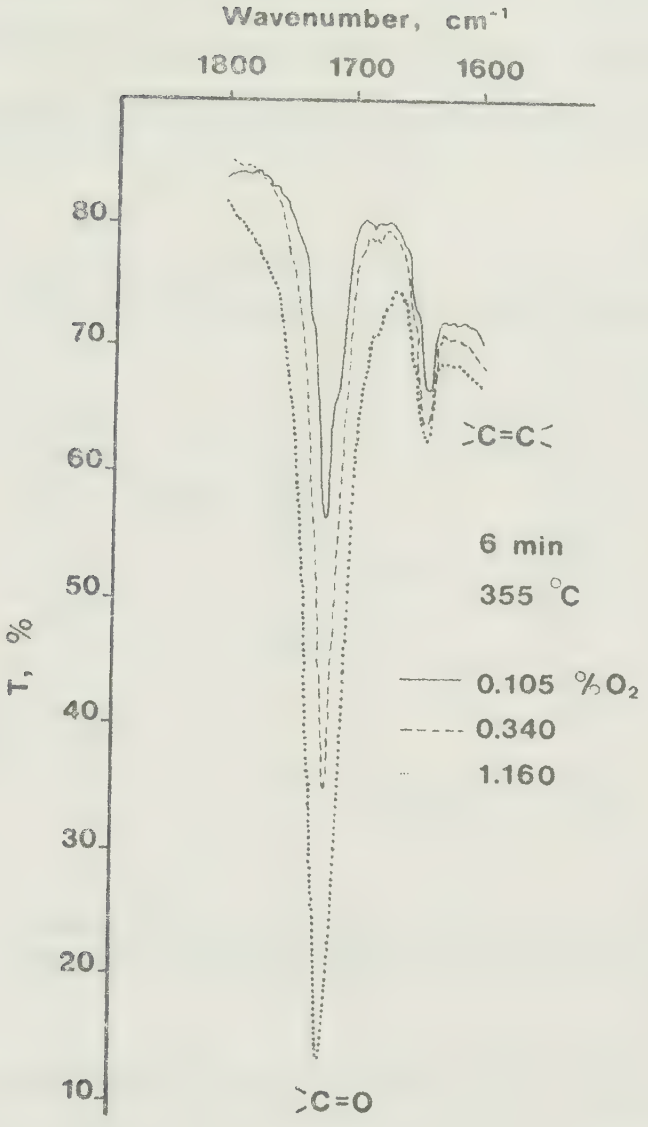


Figure 20. Infrared spectra in the range 1600-1800 cm^{-1} for samples heated for 6 min at 355°C.

The unsaturated groups were studied by IR. Like Quackenbos (61) we found that the number of carbonyl groups increased and also that the increase was relatively insensitive to temperature. The effect of oxygen content was large, however, Fig 20. The position of the carbonyl peak indicates that it should be due mainly to ketonic groups. One of the most treated samples was tested with

negative result for carboxylic groups by immersing it in 0.2 M NaOH in 95 % ethanol for 90 days (74). No changes in the carbonyl peak were observed and no peak at 1585 cm^{-1} appeared.

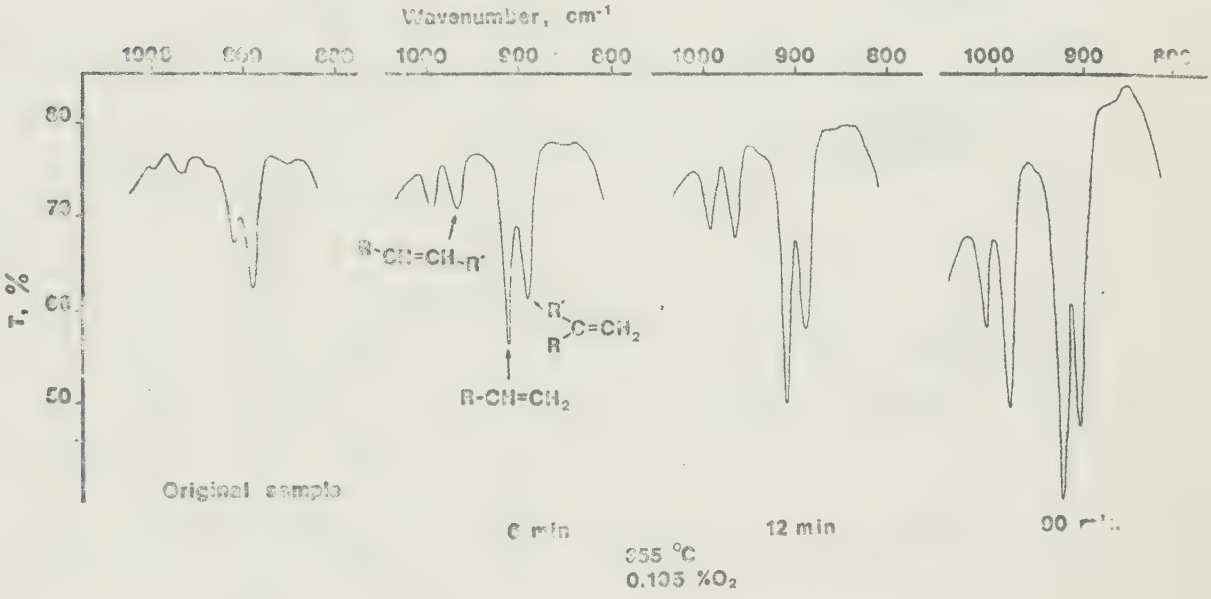


Figure 21. Infrared spectra in the range 800-1000 cm^{-1} for samples heated at 355°C in 0.105 % O_2.

Olefinic unsaturation increased with time, temperature and oxygen content. The effect of heating time is illustrated in Fig 21. It was found that the content of trans-vinylene groups was strongly affected both by temperature and oxygen content, while the content of vinyl and vinylidene groups was very sensitive to temperature changes, but only slightly affected by changes in oxygen content.

No hydroxylic groups were formed. A broad C-O band centered at

1080 cm^{-1} was found to increase with time, temperature and oxygen content.

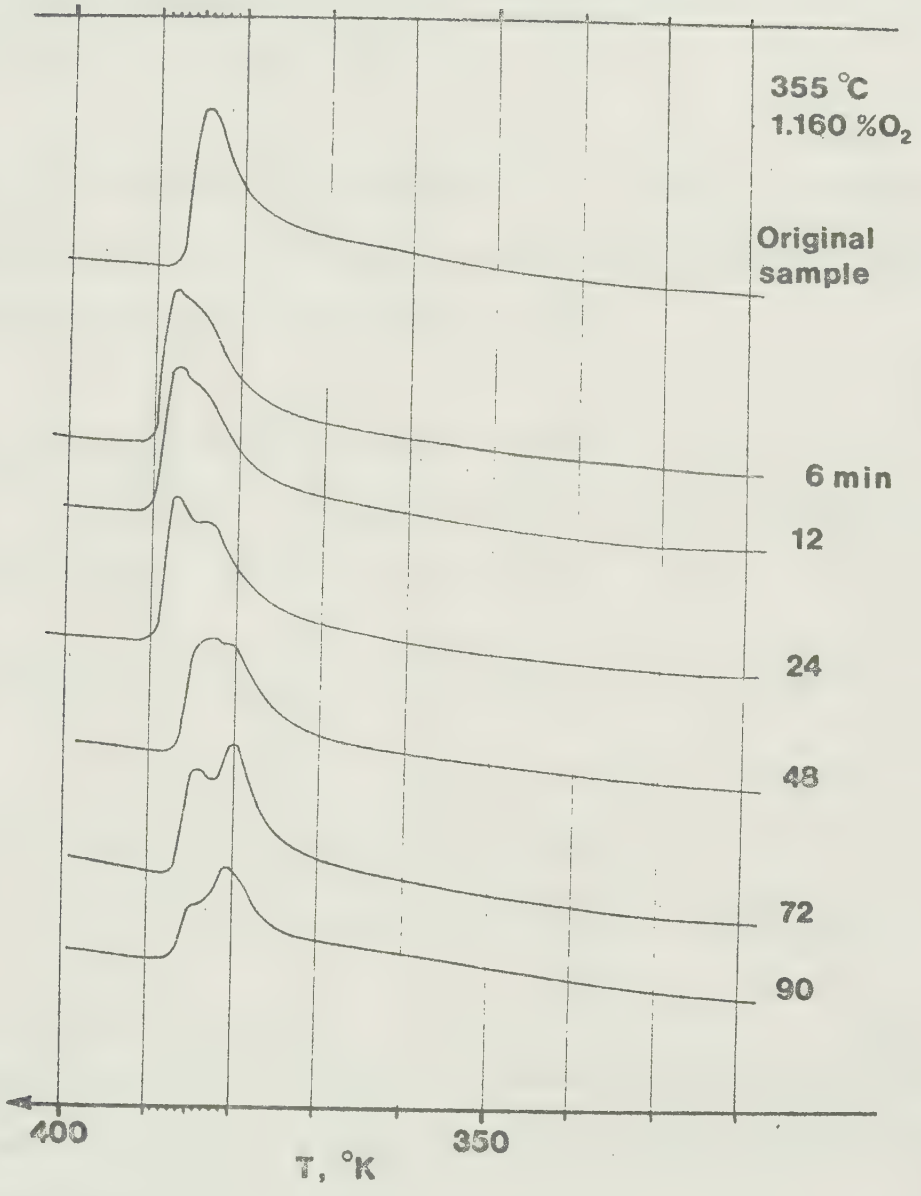


Figure 22. DSC thermograms for samples heated at 355°C in 1.16 % O_2

The DSC thermograms for samples heated at 355°C in 1.16 % O_2 are shown in Fig 22. The changes up to 24 min are generally the same as for pure thermal degradation, Fig 12. A longer treatment results in a new peak at 380°C, the peak at 387°K

disappears and the area under the curve is reduced (to about 60 % of the original after 90 min). The rate of changes decreased with decreasing heating temperature and oxygen content and was negligible at 284 and 315°C.

Due to the restricted accessability of oxygen, we considered it necessary to take both thermal and thermo-oxidative reactions into account when interpreting our data.

The thermo-oxidative reactions suggested to be operative under the conditions used, are mainly based on the reactions of organic peroxy radicals reviewed by Fish (75).

The following designations are used:

R, R′ = alkyl groups

R″ = hydrogen or alkyl groups

R‴· = alkyl radical, RO·, ROO·, HO·, or HOO·

The initiation reactions 1-3 are considered to be the most probable starting reactions even when oxygen is present. If oxygen is available the radicals formed will immediately undergo reaction 16.

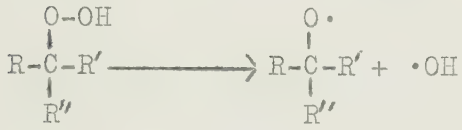
$$R\text{-}\underset{\displaystyle R''}{\overset{\displaystyle \cdot}{C}}\text{-}R' + O_2 \longrightarrow R\text{-}\underset{\displaystyle R''}{\overset{\displaystyle O\text{-}O\cdot}{C}}\text{-}R' \qquad (16)$$

Hydroperoxides may then be formed both by inter- and intramolecular hydrogen abstraction.

Intermolecular hydrogen abstraction is shown in reaction 17.

(17)

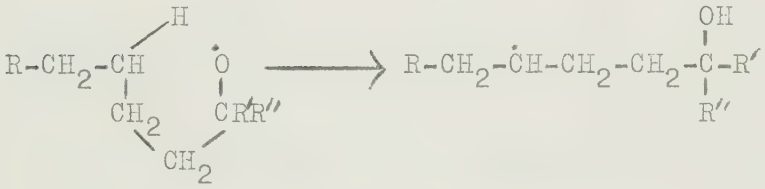
Possible subsequent reactions are:



(18)

(19)

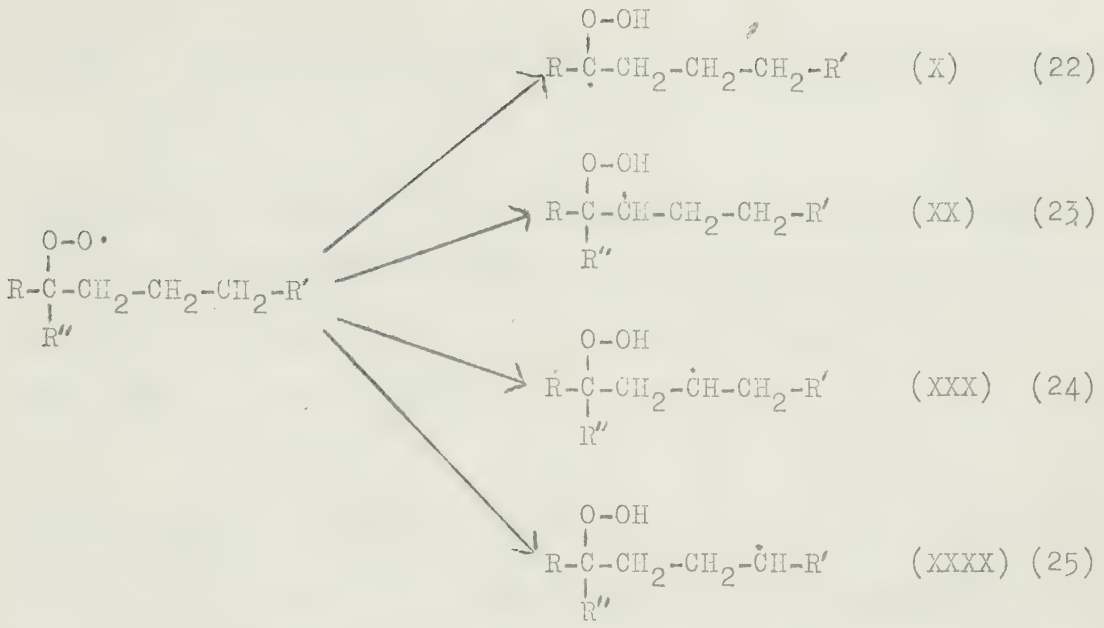
(20)



(21)

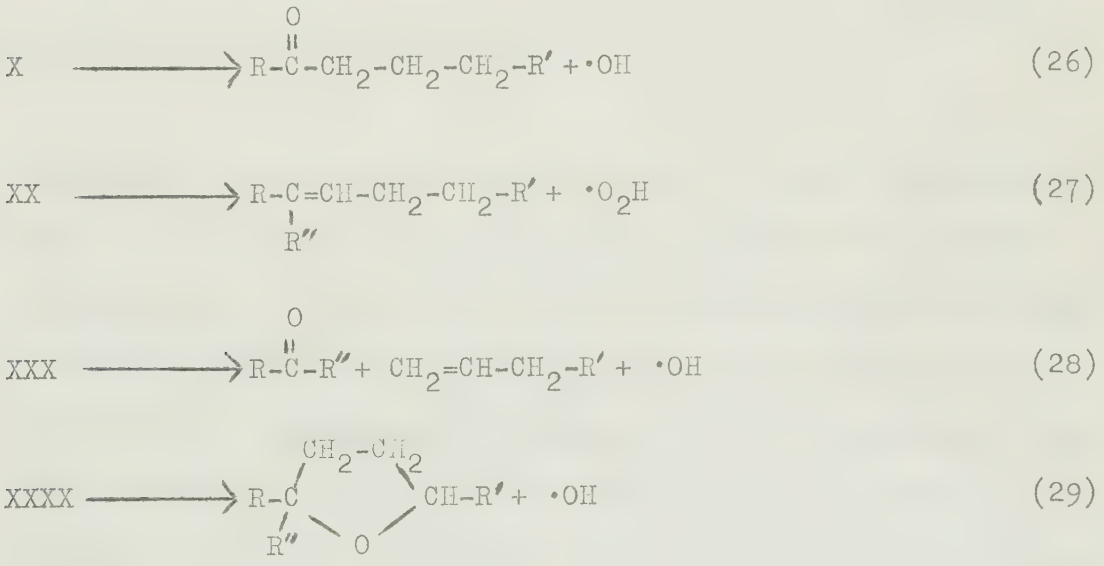
Aldehydes, ketones and hydroxy compounds are formed and chain scission occurs. Due to their labile hydrogen, aldehydes formed are considered to undergo rapid hydrogen abstraction and subsequent carbon monoxide loss under the prevailing conditions.

Intramolecular hydrogen abstraction may proceed by different routes.



Since reaction 22 involves a strained four-membered ring in the hydrogen abstraction step, it is considered to be relatively unimportant.

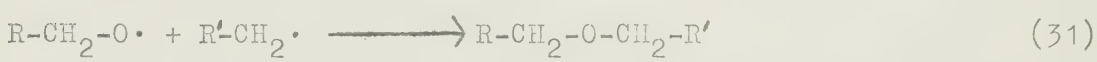
The most probable subsequent reactions will result in e.g. chain scission and the formation of vinyl and trans-vinylene groups and tetrahydrofuran derivatives (THF-derivatives).



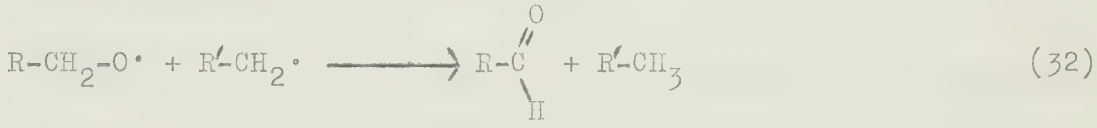
(30)

Reaction 30, together with the doubling of the radical concentration after each intermolecular hydrogen abstraction sequence (reactions 16, 17, and 18), will result in the well-known "autoxidation".

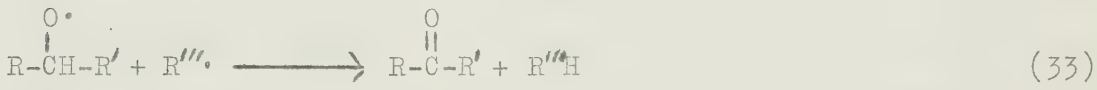
The termination reactions, involving alkoxy radicals considered bo be of importance in the thermo-oxidative degradation of PE under our conditions, are reactions 31-33.



(31)



(32)



(33)

Disproportionation, reactions 32 and 33, must be considered most probable at the temperatures used.

As discussed above, chain scission and molecular enlargement reactions compete in the purely thermal degradation of LDPE. Introduction of oxygen will cause the chain scission reactions to increase drastically as evidenced by a high weight loss (Fig 19) and an appreciable increase in the low molecular weight end of the MWD:s (Fig 14 and 15). However, even in the presence of oxygen, molecular enlargement will occur. The complex changes

in the high molecular weight tail of the MWDs, the increase in the degree of LCB (Fig 18), and the presence of insoluble material are all results of such reactions. Other significant effects of oxygen are the formation of substantial amounts of carbonyl and trans-vinylene groups and the formation of conjugated systems evidenced by discolouration.

The molecular enlargement observed is proposed to be mainly due to a combination of alkyl radicals, reactions 12 and 13, since the alkoxy radicals are considered to mainly undergo disproportionation, reactions 32 and 33.

The presence of oxygen and relatively long reaction times are prerequisites for discolouration. No discolouration is observed even if PE is degraded down to a mobile liquid under vacuum or inert atmosphere (51). We have found (76) that heating the same LDPE resin in air at 180°C for 30 min results in a large increase in carbonyl content, but no additional olefinic unsaturation and no discolouration. Since heating at 284°C to the same carbonyl content results in discolouration and an appreciable increase in the amount of trans-vinylene groups, we correlate the formation of discolouration with the increase in transvinylene groups. Formation of internal carbonyl groups has been suggested (77, 78) to proceed according to reactions 17, 18, and 33, involving intermolecular hydrogen abstraction. Formation of trans-vinylene groups is suggested to proceed via intramolecular hydrogen abstraction, reactions 23 and 27. Fish (75) has shown that the

importance of the intramolecular hydrogen abstraction will successively increase with temperature. This temperature dependence may explain why no formation of trans-vinylene groups was observed at 180°C while carbonyl groups were formed at both temperature levels.

The observed increase in ether groups is supposed to be due to the formation of THF-derivatives according to reactions 25 and 29.

The formation of low molecular weight material in the MWD:s is suggested to be accomplished via the reactions including random chain scission, reactions 10 a-c, 19 and 24.

Volatiles are considered to be formed both by back-biting and subsequent β-scission, reactions 5, 6, 7, 8, and 19 and by volatalization of low molecular weight material formed by random chain scission. The last suggestion is based on the fact that material with molecular weight in the order of 500 is often formed, Fig 15.

The changes in the DSC thermograms, Fig 22, could not be correlated with the number of methyl groups per 1000 C. The increase in peak melting temperature to 387°K and the redevelopment of the peak at 384°C are suggested to be explained by the successive increase in low molecular weight material. The increased amount of chain ends, olefinic unsaturation and oxygen-containing groups

is suggested to account for the disappearance of the high melting peak after 48 min of heating. The lower melting peak at 380°K, which simultaneously develops, may be due to a highly ordered structure containing carbonyl groups (79).

As discussed above for the purely thermal degradation, the changes in intrinsic viscosity (Fig 13) are due to changes both in average molecular weight and in degree of LCB.

Conclusions

Increased heating temperature and oxygen content during thermo-oxidative degradation of LDPE above 284°C increase the formation of:

low molecular weight material
long chain branches
volatile products
carbonyl, ether, and olefinic groups
conjugated sequences
insoluble material.

Chain scission accounts for the formation of low molecular weight material and volatiles. Molecular enlargement accounts for the formation of high molecular weight material, LCB and ultimately the formation of insoluble material.

Transvinylene and ether groups are suggested to be formed via

intramolecular hydrogen abstraction while carbonyl groups form via intermolecular hydrogen abstraction by peroxy radicals. Discolouration is correlated to the formation of trans-vinylene groups and the formation of conjugated sequences.

ACKNOWLEDGEMENTS

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